

UNIVERSAL  
LIBRARY

**OU\_162326**

UNIVERSAL  
LIBRARY



OSMANIA UNIVERSITY LIBRARY

Call No. 537.53/B56 X Accession No. 9942

Author Broglie, H. De

Title

X-Rays 1925  
This book should be returned on or before the date last marked below.

---





## **X - R A Y S**



# X-RAYS

BY

MAURICE DE BROGLIE

TRANSLATED BY

J. R. CLARKE

M.Sc., F.Inst.P.

ASSISTANT LECTURER IN PHYSICS, UNIVERSITY OF SHEFFIELD

WITH SEVEN PLATES AND THIRTY-NINE



METHUEN & CO. LTD.  
36 ESSEX STREET W.C.  
LONDON

*First Published in 1925*

PRINTED IN GREAT BRITAIN

## TRANSLATOR'S NOTE

**A**LTHOUGH this book was only published towards the end of 1922, the rapid growth of the subject of X-rays made both revision and addition desirable. M. de Broglie has been good enough to furnish the necessary alterations for this edition.

I desire to take this opportunity to express my thanks to Professor S. R. Milner, F.R.S., for reading the manuscript of the translation and for many valuable suggestions.

J. R. CLARKE

THE UNIVERSITY,  
SHEFFIELD



## AUTHOR'S PREFACE

**I**T appeared desirable at the commencement of this book to recall some of the essentials of Bohr's theory. The details of this theory will be treated in a special monograph, and it is not intended to undertake here a full investigation thereof. Nevertheless, though some of the conceptions of Bohr and Sommerfeld (such as plane atoms, the existence of complicated and interlaced orbits, etc.) are open to criticism, the introduction of energy levels and Bohr's rules for calculating the emission frequencies when an electron passes from one level to another provides a conception admirably adapted to the description of the phenomena, as well as a language which is very convenient for expressing the laws.

In addition, it is essential that the part played by quanta in the physics of high-frequency radiations should be clearly understood.

The very numerous experimental facts referred to in the book can be co-ordinated and classified in a remarkable manner if the point of view developed in the next chapter is assumed.

Since the publication of the French edition of this book, the branch of physics with which it deals has

made still further progress. In several cases values given by more recent measurements have been added to the tables, and various additions have been made to the text, notably with reference to Compton's discoveries. In addition, two appendices have been devoted to the refractive index and total reflection of X-rays, and to the progress made in the domain of  $\gamma$ -rays.



# CONTENTS

	PAGE
PREFACE . . . . .	vii

## CHAPTER I

### PART I

#### BOHR'S THEORY

1. Natural order of the elements . . . . .	I
2. Energy levels and critical frequencies . . . . .	I
Distribution of the electrons between the levels . . . . .	4
3. The principle of combination and series of lines . . . . .	7
Series of lines . . . . .	8
4. Formulæ of the theories of Bohr and Sommerfeld . . . . .	9
Sommerfeld's theory . . . . .	II
5. Moseley's law . . . . .	12

### PART II

1. The occurrence of quanta in radiation phenomena . . . . .	13
2. Undulatory radiations . . . . .	14
3. Corpuscular radiations . . . . .	18
4. Reaction of matter to radiation . . . . .	19
5. Secondary or fluorescent rays . . . . .	20
6. Ionisation and resonance potentials . . . . .	22

## CHAPTER II

#### THE SCATTERING OF X-RAYS BY MATTER

1. Diffraction of X-rays by crystals . . . . .	24
2. Determination of the absolute value of the reticular distances of crystals and of the wave-lengths of X-rays . . . . .	27
Remarks on the value of $d$ ; the limitation which it sets in the application of crystalline diffraction . . . . .	34
Confirmations of the values found for wave-lengths . . . . .	36
3. More complete theory of the scattering of X-rays. Influence of thermal agitation . . . . .	37

	PAGE
4. Influence of the number and disposition of the electrons in the atom . . . . .	39
5. The coefficient of reflection of X-rays from crystalline faces . . . . .	40
Electronic connection between the atoms in the crystal . . . . .	43
Abnormal absorption . . . . .	45
6. Absorption resulting from scattering . . . . .	45
7. Change of wave-length by scattering . . . . .	48

## CHAPTER III

### THE ABSORPTION OF X-RAYS BY MATTER

1. Coefficients of absorption . . . . .	53
2. Absorption corresponding to fluorescence . . . . .	54
3. Variation of the absorption coefficient of an element with the wave-length . . . . .	56
4. Verification of Bragg and Peirce's law . . . . .	57
5. The wave-lengths of the absorption discontinuities . . . . .	62
6. The fine structure of the discontinuities . . . . .	65
Theoretical predictions of the number of absorption limits . . . . .	65
Regular and irregular doublets . . . . .	66
7. K discontinuities . . . . .	67
J bands . . . . .	69
8. L discontinuities . . . . .	70
9. M discontinuities . . . . .	73
10. Discontinuities of higher orders, N, O, P . . . . .	73
11. The existence of fringes in the immediate neighbourhood of the absorption discontinuities . . . . .	74
12. The influence of the chemical state on the frequencies of the absorption discontinuities of the light elements . . . . .	75
13. Theoretical predictions concerning absorption phenomena . . . . .	76
Theoretical calculation of the coefficient of Bragg and Peirce's law . . . . .	78
14. The special behaviour of the atomic absorption coefficient with long wave-lengths . . . . .	80

## CHAPTER IV

### PART I

#### THE CONTINUOUS SPECTRUM

1. The emission of X-rays . . . . .	83
2. The limit of the continuous spectrum emitted by an anticathode bombarded by cathode rays of given energy . . . . .	84
Measurement of $h$ . . . . .	85
3. The distribution of the energy between the wave-lengths of the continuous spectrum . . . . .	87

# CONTENTS

xi

PAGE

4. The variation of the intensity of the continuous spectrum with the element used as anticathode, and the efficiency of an X-ray tube . . . . .	89
The variation of the emission with the nature of the anticathode . . . . .	90
The variation of the emission with the applied voltage . . . . .	91
The efficiency of an X-ray tube . . . . .	91
5. Properties of the radiation emitted in various directions ; Polarisation of X-rays . . . . .	91
Polarisation . . . . .	94
The variation of the intensity and the quality of the rays with the azimuth . . . . .	95

## PART II

### LINE SPECTRA

1. The emission of characteristic lines . . . . .	97
The excitation of the lines of the L series . . . . .	99
2. The intensity of emission of characteristic lines . . . . .	100

### DATA CONCERNING THE LINES OF THE VARIOUS SERIES FOR ALL THE ELEMENTS

3. Lines of the K series . . . . .	102
4. Lines of the L series . . . . .	107
5. Lines of the M series and of the N series . . . . .	110
Note . . . . .	111
6. Moseley's law for emission lines . . . . .	116
7. Experimental basis of the principle of combination . . . . .	117
8. The principle of selection . . . . .	117
9. The excitation of secondary rays by primary X-rays . . . . .	118
10. The emission of X-rays of very long wave-length and the continuity between these rays and the extreme ultra-violet . . . . .	121
11. Analysis by X-ray spectra . . . . .	127
12. The reflection and the diffraction by a slit of very soft X-rays : total reflection . . . . .	128
13. Analogy between optical spectra and X-ray spectra . . . . .	129

## CHAPTER V

### SPECTROGRAPHS AND SPECTROMETERS

1. General indications . . . . .	134
2. The ionisation method . . . . .	136
3. The photographic and rotating crystal method . . . . .	139
4. Special arrangements for rays of short and long wave-lengths . . . . .	141
5. Curved crystalline sheets . . . . .	145

	PAGE
6. Measurements of wave-length . . . . .	146
7. Dispersion: resolving power . . . . .	149
8. The photography of absorption spectra . . . . .	150
9. The use of reinforcing screens . . . . .	152
10. Microscopic crystals and crystalline powders . . . . .	153
11. Diagrams of non-crystalline substances . . . . .	156

### SOURCES OF X-RAYS

12. New hot cathode tubes . . . . .	158
Coolidge tubes . . . . .	158
The Lilienfeld tube . . . . .	158
The Müller "electron" tube . . . . .	160
13. Constant voltage apparatus . . . . .	161

## CHAPTER VI

### PART I

#### SECONDARY $\beta$ -RAYS DUE TO X-RAYS

1. The X-ray photoelectric phenomenon . . . . .	165
2. Investigations on the magnitude and the distribution of the velocities possessed by the electrons emitted under the action of X-rays . . . . .	165
3. Experimental investigation of the magnetic spectra of secondary $\beta$ -rays, and the laws of the phenomenon . . . . .	168
4. Magnetic corpuscular spectra: the analysis of the levels, and the transposition of X-ray spectra . . . . .	171
5. C. T. R. Wilson's experiment . . . . .	176

### PART II

#### $\gamma$ -RAYS

1. The measurement of $\gamma$ -rays by crystalline diffraction . . . . .	177
2. Determination of the wave-length of $\gamma$ -rays by means of their secondary $\beta$ -rays and of the works of extraction . . . . .	180
CONCLUDING REMARKS . . . . .	185

### APPENDICES

1. The refraction and total reflection of X-rays . . . . .	191
The existence of a refractive index for X-rays . . . . .	191
Anomalous dispersion . . . . .	192
Total reflection . . . . .	193
Refraction . . . . .	193
2. $\beta$ -ray and $\gamma$ -ray spectra . . . . .	195
SUBJECT INDEX . . . . .	199
AUTHOR INDEX . . . . .	202

# LIST OF PLATES

	FACING PAGE
Plate 1 . . . . .	64
„ 2 . . . . .	112
„ 3 . . . . .	128
„ 4 . . . . .	140
„ 5 . . . . .	144
„ 6 . . . . .	154
„ 7 . . . . .	176

Tables XXVB and XXVI . . . . . *between pages 116 and 117*



# X-RAYS

## CHAPTER I

### PART I

#### BOHR'S THEORY

**1. Natural order of the elements.**—The phenomena of X-rays are almost exclusively atomic, i.e. only the nature of the chemical elements present in the substance in the interior of which the effects of rays are produced is concerned, and not their state of chemical combination nor their physical state, at least to a first approximation. It is necessary, therefore, to commence by saying a few words about the structure of the elements.

It is well known that these have been classified in the order of increasing atomic weight by a classification known as Mendéléeff's table, or the periodic table of the elements. Various considerations, developed particularly by Rydberg and van den Broek, have led to a whole number  $N$  being regarded as the true variable of which the properties of the elements are a function. The atomic number, or better, the atomic numeral,  $N$ , represents the position of the element in the natural order, and also indicates the number of elementary positive charges possessed by the nucleus of the atom.

The great natural law discovered by Moseley by providing an exact means of assigning to each element, without hesitation, its correct atomic number, has given a very solid basis to the conception introduced by van den Broek, and has attached to it a fundamental importance.

**2. Energy levels and critical frequencies.**—Bohr's theory supposes the atom of an element of atomic number  $N$  (i.e.

occupying the  $N$ th position in the natural order of the elements) to be composed of a nucleus possessing a total positive charge equal to  $+Ne$ , surrounded by swarm of  $N$  electrons arranged in a definite manner.

We shall especially adopt Bohr's conception that these  $N$  electrons are divided into several groups, characterised by the work which must be done to extract an electron of the group from the atom. It is immaterial for our purposes whether the electrons of a particular group be considered to be distributed on a layer, on a level, or moving in a series of orbits; the essential thing is that to each group must be assigned a definite amount of "work of extraction." Henceforward the word level will be used in preference to any other.

Successive levels, counted from the nucleus, have been designated by custom, by the letters K, L, M, . . . , and when it is desired to refer to a kind of fine structure of a level, the neighbouring levels belonging to the same layer are denoted by the letters  $L_1, L_2, L_3, \dots M_1, M_2, M_3, \dots$ . The works of extraction  $W_1, W_2, W_3, \dots$  which characterise these levels, will obviously decrease in the sense K, L, M, . . . since they are concerned with the separation of two charges of opposite signs from initial positions which are closer together the nearer the level considered is to the centre.

Using the notation of the quantum theory, we make a frequency correspond to an energy by writing that this energy is equal to the frequency multiplied by Planck's constant  $h$ . Thus for each level there can be defined a frequency  $\nu$  related to the work of extraction  $W$  by the expressions

$$\nu = \frac{W}{h} \text{ or } \nu_L = \frac{W_L}{h} . . .$$

This being assumed, it is desirable to recall that the fundamental hypotheses of Bohr's theory are as follows: A spectral line is emitted by an atom when an electron passes from one level to another nearer to the nucleus; for



NATURAL ORDER OF THE ELEMENTS.

I	II	III	IV	V	VI	VII	VIII
<sup>1</sup> H = 1.008							
<sup>2</sup> He = 3.99	<sup>3</sup> Li = 6.94	<sup>4</sup> Be = 9.1	<sup>5</sup> B = 11.0	<sup>6</sup> C = 12.0	<sup>7</sup> N = 14.01	<sup>8</sup> O = 16.00	<sup>9</sup> F = 19.0
<sup>10</sup> Ne = 20.2	<sup>11</sup> Na = 23.00	<sup>12</sup> Mg = 24.32	<sup>13</sup> Al = 27.1	<sup>14</sup> Si = 28.3	<sup>15</sup> P = 31.04	<sup>16</sup> S = 32.06	<sup>17</sup> Cl = 35.46
<sup>18</sup> <u>A = 39.88</u>	<sup>19</sup> K = 39.10	<sup>20</sup> Ca = 40.07	<sup>21</sup> Sc = 44.1	<sup>22</sup> Ti = 48.1	<sup>23</sup> V = 51.0	<sup>24</sup> Cr = 52.0	<sup>25</sup> Mn = 54.93
	<sup>29</sup> Cu = 63.57	<sup>30</sup> Zn = 65.37	<sup>31</sup> Ga = 69.9	<sup>32</sup> Ge = 72.5	<sup>33</sup> As = 74.96	<sup>34</sup> Se = 79.2	<sup>35</sup> Br = 79.92
<sup>36</sup> Kr = 82.92	<sup>37</sup> Rb = 85.45	<sup>38</sup> Sr = 87.63	<sup>39</sup> Y = 88.7	<sup>40</sup> Zr = 90.6	<sup>41</sup> Nb = 93.5	<sup>42</sup> Mo = 96.0	<sup>43</sup> Ru = 101.7
	<sup>47</sup> Ag = 107.88	<sup>48</sup> Cd = 112.40	<sup>49</sup> In = 114.8	<sup>50</sup> Sn = 118.7	<sup>51</sup> Sb = 120.2	<sup>52</sup> Te = 127.5	<sup>53</sup> I = 126.92
<sup>54</sup> Xe = 130.2	<sup>55</sup> Cs = 132.81	<sup>56</sup> Ba = 137.37	<sup>57</sup> La = 139.0	<sup>58</sup> Ce = 140.25	<sup>59</sup> Pr = 140.6	<sup>60</sup> Nd = 144.3	<sup>61</sup> Sa = 150.4
<sup>67</sup> Ho = 163.5	<sup>68</sup> Er = 167.7	<sup>69</sup> Tm = 168.5	<sup>70</sup> Yb = 173.5	<sup>71</sup> Lu = 175.0	<sup>72</sup> Ct = ?	<sup>73</sup> Ta = 181.5	<sup>74</sup> W = 184.0
	<sup>79</sup> Au = 197.2	<sup>80</sup> Hg = 200.6	<sup>81</sup> Tl = 204.0	<sup>82</sup> Pb = 207.20	<sup>83</sup> Bi = 208.0	<sup>84</sup> Po = 210.0	<sup>85</sup> Os = 190.9
<sup>86</sup> Em = 222.0	<sup>87</sup>	<sup>88</sup> Ra = 226.0	<sup>89</sup> Ac = 227	<sup>90</sup> Th = 232.15	<sup>91</sup> UX <sub>2</sub> = 234	<sup>92</sup> U = 238.2	<sup>93</sup> Ir = 193.1
							<sup>94</sup> Pt = 195.2
							<sup>95</sup> Pa = 106.7
							<sup>96</sup> Fe = 55.84
							<sup>97</sup> Co = 58.97
							<sup>98</sup> Ni = 58.68
							<sup>99</sup> Rh = 102.9
							<sup>100</sup> Pd = 106.7

example, from the M level to the K level. This spectral line (which is emitted with an energy  $h\nu$ ) possesses a frequency defined by the equation

$$\nu = \nu_K - \nu_M.$$

Conversely, the transference of an electron from a level to another which is less central, for example, from K to M, should correspond to the absorption of a definite frequency. However, as will be seen later, this does not appear to take place, in general, with X-rays. When an electron is removed from a level it seems almost always to be completely extracted from the atom; in the case where the level concerned is, for example, the L level, this corresponds to the transference of an electron from this level to infinity with the absorption of a frequency

$$\nu_L - \nu_\infty$$

or simply

$$\nu_L$$

since

$$\nu_\infty = \frac{W_\infty}{h} = 0.$$

It is only by absorbing a frequency at least equal to  $\nu_L$  that the electron from the L ring can be extracted from the atom. This frequency  $\nu_L$  may be considered, therefore, as being a critical absorption frequency, or the frequency of an absorption discontinuity corresponding to the L level.

*Distribution of the electrons between the levels.*—The  $N$  electrons of the atom of atomic number  $N$  are considered to be distributed amongst the Bohr levels of the atom; how does this distribution take place?

There are reasons to believe that as  $N$  increases, i.e. as the natural order of elements is followed, every time an inert gas is passed a new layer is formed, which is filled with electrons one by one. The number of layers fully charged with electrons is thus equal to the number of inert gases passed over as the atomic number is changed from 1 to  $N$ .

It is obviously difficult to be much more precise, but

the following distribution,\* based principally on considerations of a chemical nature, has been proposed [7].

TABLE I

Atomic Number.	Element.	Number of Electrons in Layers Full of Electrons.						
		K.	L.	M.	N.	O.	P.	Q.
2	He	2	—	—	—	—	—	—
10	Ne	2	8	—	—	—	—	—
18	A	2	8	18	—	—	—	—
36	Kr	2	8	18	8	—	—	—
54	Xe	2	8	18	18	8	—	—
86	Em	2	8	18	32	18	8	—
92	U	2	8	18	32	18	8	6

Whatever the arrangement, a point is reached when the  $N$  electrons are all used, being divided between the levels, for example, the K, L, M, N, levels; according to Bohr's theory the remaining levels O, P, Q, . . . are considered to exist only as virtual levels to which electrons can move, but which in the normal state of the atom are unoccupied.

It appears that the normal state of the atom can be defined in this way. Each of the levels can contain a certain maximum number of electrons; when the  $N$  electrons are so placed that the most central levels are all full, the atom is in a state of minimum potential energy to which it will always tend to return.

If an electron is missing from one of the rings which is normally full, its place will tend to be taken by an electron from one of the neighbouring rings, or from outside the atom, with the emission of radiation according to Bohr's hypotheses.

The outer levels which contain electrons can be called peripheral or superficial levels, or else optical or chemical levels, and are characterised by the lowest work of extraction. The electrons which constitute them, being situated at the surface of the atom, are subject to external forces, such as those due to collision, chemical forces, cohesive forces, etc.,

\* N. Bohr, L. de Broglie, and A. Dauvillier. See also E. C. Stoner, *Phil. Mag.*, 1924, **48**, 286; and L. de Broglie and A. Dauvillier, *ibid.*, 1925, **49**, 752.

which can easily displace them or even tear them completely from the atom.

These superficial levels, therefore, may not have their full complement of electrons, especially when the atom is subjected to intense forces. If one or more electrons are missing in this way the atom is said to be "ionised," and bears an excess positive charge; it will be a positive mono- or multi-valent ion. It may happen also that a superficial electron without being completely detached from the atom may be carried to a level farther from the nucleus than the last normally full level; it will then be in an only slightly stable condition, since its work of extraction will be very small.

This can be understood more clearly by considering Bohr's theory of the lines in the Balmer series of hydrogen. In this case there is only one electron and in the most stable state this will be on the K level; but other levels exist in the virtual state and there will be some slightly abnormal atoms of hydrogen which will have their electrons on the L, M, N, . . . levels. When the electron jumps from one of these levels to another the lines of the optical spectrum are emitted. The farther the virtual level considered is from the nucleus the more improbable does it become that the hydrogen atom will be able to keep the electron on this level, although in the absence of external forces, for example in the case of hydrogen at very low temperature and pressure, the more remote levels can be more easily called into play. The presence of the higher terms of the Balmer series in the spectra of the nebulae can be explained in this way.

It should be mentioned also that, when the matter is considered more closely, the position of all the levels must vary very slightly when one of the electrons is moved from its normal position. The central levels are almost unaffected, at least in the heavy atoms, by the degree of superficial ionisation, but, actually, the atom is capable of existing in a very large number of states, characterised by levels which are not rigorously identical. When the superficial

levels of strongly disturbed atoms are considered, this leads to the possible rays emitted being very complex; such a condition obtains, for example, in the luminous spark spectra.

### 3. The principle of combination and series of lines.—

Bohr's fundamental hypothesis states that a line is emitted when an electron jumps from one level to another, the frequency of the line being equal to the difference between the critical frequencies of the levels concerned. Thus the possible number of lines\* is equal to the number of ways in which the levels can be arranged two at a time. This can be called the principle of combination of levels (Kossel),

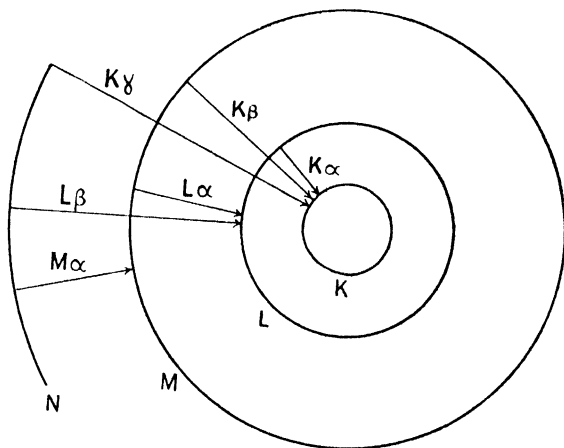


FIG. 1.

and a list of predicted lines can be obtained by making a "double-entry" table connecting the levels of departure and arrival, as in Table XXVI.

The levels can also be represented as in Fig. 1, the lines being indicated by arrows joining the levels concerned. It can be seen from this figure that by adding or subtracting the frequencies of two lines the frequency of another line is obtained.

\* All these lines do not exist; the principle of selection (see p. 117) predicts that there will be, among the possible combinations, certain lines which are effectively realisable.

*Series of lines.*—Among the lines predicted those which have the same level of arrival can be considered together, because their emission is conditioned by the same initial phenomenon, namely, the existence of an empty space on this level. Experiment shows that these lines actually are made possible by the same mechanism and form natural groups (p. 102). The series and the lines which belong to it are designated by the letter appropriated to the level of arrival. The K series, for example, is composed of lines of frequencies :

$$\begin{aligned}\nu_{KL} &= \nu_K - \nu_L \\ \nu_{KM} &= \nu_K - \nu_M \\ \nu_{KP} &= \nu_K - \nu_P.\end{aligned}$$

These different frequencies are arranged in order of increasing magnitude and they tend, as the terms subtracted become less and less, to a frequency limit, which is exactly the critical frequency,  $\nu_K$ , of the level of arrival. It is customary to denote the line of lowest frequency, i.e. that of which the level of departure is nearest to the level of arrival, by the letter  $\alpha$ , and the others by  $\beta$ ,  $\gamma$ , . . . , but this rule is not absolute. In general also the first lines  $\alpha$ ,  $\beta$ , of a series are the most intense, as would be expected if a vacant place were supposed to be most probably filled at the expense of the nearest levels.

When an exciting radiation, falling on a small quantity of matter which contains a large number of atoms, is able to detach an electron from the K ring of a certain number of these atoms, it is natural to expect that in some of the atoms the space will be filled by an electron from, say, the L ring, with the emission of the  $K\alpha$  line ; the space thus created on the L ring will be filled at the expense of the M ring, with emission of the  $L\alpha$  line. In other atoms an electron of the M ring will jump direct to the K ring, emitting the  $K\beta$  line, and so on.

The emission of the series is thus a statistical phenomenon resulting from the actions which are produced in a large number of disarranged atoms, and the intensity of a line is

a measure of the probability of the particular combination of levels with which it is concerned.

Let us consider, for an instant, the high terms of a series, the departure levels of which belong to the outer parts of the atom. They will have frequencies very near to the critical frequency of their level of arrival, and their existence will depend on the real or virtual state of the outer departure levels. The number of lines will be greater, therefore, for elements of high atomic weight in which the levels full of electrons are themselves more numerous. The exterior forces, chemical, cohesive, etc., which modify the superficial levels, will be able, in addition, to exert an appreciable effect on the higher terms of the series.

Thus it is the lines near to the critical discontinuity which are affected by the action of external agents. These lines, therefore, will share with the lines of luminous spectra certain properties which are not possessed by the lines arising from the deeper levels, which are practically independent of external forces.

The foregoing applies to all the series of radiations emitted by an atom of atomic number  $N$ . The question arises how these different lines behave when the atomic number changes. To answer this question it is necessary to consider Bohr's theory in more detail.

#### 4. Formulæ of the theories of Bohr and Sommerfeld.—

Let us consider a nucleus bearing a positive charge  $+Ne$  and an electron, of charge  $-e$  placed near to it. Employing the principles of the quantum theory and assuming the electronic orbits to be circles with the nucleus as centre, Bohr was led to conceive that only a certain number of orbits of radii  $r_K, r_L, r_M, \dots$  corresponding to the levels referred to above, were possible. These radii are given by the formula

$$r = \frac{n^2 h^2}{4\pi^2 e^2 m N} \quad . \quad . \quad . \quad . \quad (1)$$

where  $h$  is Planck's constant,  $e$  the elementary electronic charge,  $N$  the atomic number,  $m$  the mass of an electron,

and  $n$  a whole number which may have the values 1, 2, 3, 4, . . . corresponding to the radii  $r_K, r_L, r_M, r_N, \dots$

The work of extraction necessary to take an electron from a particular level to infinity will be

$$W = \frac{2\pi^2 m N^2 e^4}{h^2 n^2}$$

or 
$$W = \frac{h\nu_0 N^2}{n^2} \quad . \quad . \quad . \quad . \quad (2)$$

if 
$$\nu_0 = \frac{2\pi^2 m e^4}{h^3}$$

a value which is equal, to a very close approximation, to Rydberg's fundamental frequency.

Thus we have

$$W_K = \frac{h\nu_0 N^2}{1^2}; \quad W_L = \frac{h\nu_0 N^2}{2^2}; \quad \dots \quad . \quad (3)$$

for the works of extraction of the various levels.

The frequencies  $\nu_K, \nu_L$  which have been defined as equal to  $\frac{W}{h}$  will therefore have the values

$$\nu_K = \frac{\nu_0 N^2}{1^2}; \quad \nu_L = \frac{\nu_0 N^2}{2^2}; \quad \dots \quad . \quad (4)$$

and the emitted radiations will be of the form

$$\nu = \nu_0 N^2 \left( \frac{1}{n^2} - \frac{1}{m^2} \right) \quad . \quad . \quad . \quad (5)$$

where  $n$  and  $m$  are whole numbers.

For example, the K series will be characterised by the equation

$$\nu = \nu_0 N^2 \left( \frac{1}{1^2} - \frac{1}{n^2} \right)$$

the L series by

$$\nu = \nu_0 N^2 \left( \frac{1}{2^2} - \frac{1}{n^2} \right).$$

This first theory of Bohr is of a very simple character; it assumes, in fact, that there are in the atom only a single negative electron and a positive nucleus, and that the orbits



are circular and in the same plane. The effect of the presence of other electrons may be allowed for by supposing that the force on the electron considered no longer depends only on  $N$  but on a function of the form  $(N - \sigma)$ . Actually the problem becomes that of  $(N + 1)$  bodies and still awaits a solution.

*Sommerfeld's theory.*—Sommerfeld has elaborated Bohr's theory by introducing the two following conceptions: (a) the orbits are not circular but elliptic; (b) the mass of the electron varies with the velocity according to the formula of relativity, which involves a change in the expression for the kinetic energy.

The elliptic nature of the orbits necessitates the consideration of two degrees of freedom, one radial and the other azimuthal, corresponding to the polar co-ordinates of the moving particle. By applying the rules of the quantum theory to each of these degrees of freedom, Sommerfeld obtains expressions for the energies of the levels which differ from those of Bohr only by the substitution of  $n + n'$  and  $m + m'$ , relative to the radial and azimuthal quantum numbers of each orbit, for the whole numbers  $n$  and  $m$ .

The general formula for the emitted radiations then becomes

$$\nu = \nu_0 N^2 \left( \frac{1}{(n + n')^2} - \frac{1}{(m + m')^2} \right) \quad . \quad . \quad (6)$$

which is identical with Bohr's formula (5) in essentials since it only contains the reciprocals of the squares of successive whole numbers.

For greater accuracy it is necessary to use  $N - \sigma$  instead of  $N$ , the force on an electron depending not only on the central charge but on the other electrons as well.

When the variation of the mass with the velocity is taken into account, each of the levels predicted by the simple theory is resolved into several neighbouring levels, separated by frequency intervals which can be expressed as functions

of what Sommerfeld has called the *fine structure constant*,

$$\alpha^2 = \frac{2\pi e^2}{ch} = 5.3 \cdot 10^{-5} \quad . \quad . \quad . \quad (7)$$

which leads to the prediction (for the L levels) of frequency differences between the duplicated levels of the form

$$\Delta\nu = \nu_0 \frac{\alpha^2}{2^4} (N - \sigma)^4 \quad . \quad . \quad . \quad (8)$$

The verification of the consequences of this elaborated theory has been one of the greatest successes of Sommerfeld's work.

*Note.*—For hydrogen we have \*

$$\Delta\nu_H = \frac{\nu_0 \alpha^2}{2^4} = 0.365 \text{ cm.}^{-1}$$

and for an element of atomic number  $N$ .

$$\Delta\nu = \Delta\nu_H (N - \sigma)^4 \quad . \quad . \quad . \quad (9)$$

For uranium ( $N = 92$ ) the  $\Delta\nu$  thus calculated is about one hundred million times greater than that for hydrogen, and it appears probable that Sommerfeld's relation continues to apply.

The law represented by the formula (9), expressed in terms of wave-lengths instead of frequencies, corresponds to a difference  $\Delta\lambda$  independent of  $N$ , since

$$\Delta\lambda = -\frac{\Delta\nu}{\nu^2} \text{ and } \nu = K(N - \sigma)^2.$$

Two spectral lines showing a frequency difference of this type are often said to form a *regular doublet*.

**5. Moseley's law.**—The fundamental law discovered by Moseley [6] may be written

$$\sqrt{\nu} = AN + B$$

$\nu$  being the frequency of a line followed through the series of the elements, and  $A$  and  $B$  being constants.

\* In good agreement with the experimental results (Paschen) deduced from the luminous spectra of hydrogen and helium.  $\Delta\nu$  is here expressed as the difference between two wave-numbers, not the difference between two frequencies. A wave-number is the reciprocal of a wave-length.

Essentially this law states that  $\sqrt{\nu}$  varies in a regular and continuous manner as  $N$  changes ; the linear form is only true to a first approximation and is only compatible with Bohr's theory so far as the frequencies of the absorption discontinuities are concerned, for which the theory gives

$$\sqrt{\nu} = A(N - \sigma).$$

The frequency of a line cannot rigorously obey a law of this form, as it is the difference between two terms of this type, in which  $\sigma$  is not the same.

## PART II

### 1. The occurrence of quanta in radiation phenomena.—

In the course of the study of the phenomena which follow, the conception of energy quanta is constantly recurring and a short consideration of it is necessary.

Planck's theory leads to the conclusion that the emission of a radiation of frequency  $\nu$ , by the atomic resonators whence it arises, does not take place continuously but in the form of definite quantities of energy equal to  $h\nu$  ; this law was proposed for the first time in the case of the continuous spectrum emitted by a black body at a given temperature.

The absorption of undulatory radiations also appears to take place by quanta ; the emission and absorption by Bohr's atom rest solely on foundations of this nature.

On the other hand, the phenomenon of photoelectricity and its converse, the excitation of a radiation by the impact of corpuscles, bring out a direct connection between the energy called into play and the frequency of the periodic radiation.

In the energy exchanges between radiation and matter, when a certain quantity of energy,  $W$ , is concerned, there nearly always results an undulatory radiation of which the frequency  $\nu$  is related to  $W$  by Planck's equation  $\nu = \frac{W}{h}$

and, conversely, a radiation of frequency  $\nu$  behaves as if it were absorbed by matter in indivisible quantities of energy,  $h\nu$ , giving to the corpuscles concerned a kinetic energy exactly equal to  $h\nu$ .

The part which the emission and wave theories have played in our ideas concerning the propagation of light is well known ; the former conception, fortified by the authority of Newton, was triumphant for a long time and was only dethroned in the nineteenth century by the influence of Fresnel and Young. The success of the undulatory theory was then thought to be definite.

At the present time, attention is being directed towards a group of phenomena which suggest afresh the emission theory, or rather, which present the facts in such a way that their aspect can be best described, sometimes in terms of the wave theory, and sometimes by means of the hypothesis of emission.

Something kinetic is to be found in undulatory radiations and something periodic in the projections of corpuscles,\* and all this makes it every day more tempting to think that a single reality is presented to us, sometimes as a kinetic and sometimes as an undulatory manifestation.

**2. Undulatory radiation.**—A luminous vibration is a periodic phenomenon characterised by a wave-length  $\lambda$ , a period  $T$ , a frequency  $\nu$ , and a velocity of propagation  $c$ , connected by the equations

$$\lambda = cT \quad \nu = \frac{1}{T} = \frac{c}{\lambda}.$$

The wave-length is the variable most generally used to define the vibrations, but for many reasons it is preferable to employ the frequency  $\nu$ , which represents the number of vibrations per second ; the wave-length, in fact, changes with the velocity of propagation, and thus is not the same in a vacuum as in a material medium. Spectroscopists realised

\* In the sense that the emission of a radiation of a period which is well defined, at least so far as its major frequency limit is concerned, corresponds to corpuscles of a particular velocity, at the instant of their collision with matter.

long ago (for example, in Balmer's formula) that the frequency is the natural variable to choose in order to obtain simple relations. Moreover, the new ideas concerning radiation make the frequency play a fundamental rôle.

On the older theory a beam of light of a certain frequency could be the seat of any amount of energy, quite independent of  $\nu$ ; but we have been led to associate with each frequency a definite quantity of energy which is called its *quantum*, and which is defined by the equation \*

$$W = h\nu,$$

the product of the frequency and the radiation constant of a black body  $h$ , the numerical value of which is  $6.55 \times 10^{-27}$  erg seconds. This constant has the dimensions of an action, i.e. an energy multiplied by a time, so that the quantum  $h\nu$  has the dimensions of energy.

It may be mentioned here that a quantum can also be defined for a particle possessing kinetic energy, and we shall see later that these considerations can be used to connect the kinetic and vibratory representations of radiations.

Wave-lengths are expressed in centimetres and frequently in Ångström units, an Ångström unit being equal to  $10^{-8}$  cm.; a frequency is the reciprocal of a time, that is, a number of vibrations per second; the quanta  $h\nu$  will be expressed in energy units, or ergs. It is, however, very convenient to express this energy in the form which it takes in the case of an electrified particle moving in an electrostatic field.

For example, if a corpuscle of charge  $e$  falls through a potential difference  $V$ , it will acquire energy equal to  $eV$ , and, by giving to  $e$  the numerical value which corresponds to the elementary charge on an electron, each quantum will correspond to a certain value of  $V$ . It is possible, in short, to express a quantum in terms of units of potential,

\* A definite quantity of energy is thus defined, which depends only on the frequency of the radiation, and has nothing to do with the intensity. A *quantum* has a double significance; it indicates both the frequency of a radiation and a certain quantity of energy carried by this frequency; it is simultaneously a quality and a quantity.

for example, in volts. Numerically,  $10^{16}$  vibrations per second is equivalent to 41·3 volts, the length  $0\cdot1\mu$  corresponds to 12·4 volts, and the length one Ångström unit to 12400 volts.\*

Thus the quantum of a radiation has been defined. In Table II the different radiations of all the known spectra are given with their appropriate characteristic magnitudes.

TABLE II

Radiation.	Frequencies per Second.	$\lambda$ (cm.).	V (volts) $V = \frac{hc}{\lambda e}$	$v$ cm./sec. $v = \sqrt{\frac{2eV}{m}}$
Electric waves— 300 metres . . .	$10^6$	$3\cdot10^4$	$4\cdot1, 10^{-9}$	$3\cdot8, 10^3$
Infra red . . .	$10^{13}$	$3\cdot10^{-3}, 30\mu$	$4\cdot1, 10^{-2}$	$1\cdot2, 10^7$
Yellow light . . .	$5\cdot10^{14}$	$6\cdot10^{-5}, 0\cdot6\mu$	2·06	$8\cdot5, 10^7$
Ultra violet . . .	$3\cdot10^{15}$	$10^{-5}, 0\cdot1\mu$	12·4	$2\cdot1, 10^8$
Very soft X-rays .	$3\cdot10^{17}$	$10^{-7}, 1\mu\mu$	1240	$2\cdot1, 10^9$
X-rays . . . . .	$3\cdot10^{18}$	$10^{-8}, 1\text{Å}$	12400	$m = 1\cdot001 m_0$
Hard X-rays . . .	$3\cdot10^{19}$	$10^{-9}, 0\cdot1\text{Å}$	124000	Mass varies with velocity
$\gamma$ -rays . . . . .	Order of $10^{21}$	Order of $10^{-11}$	Order of a million and above	

Starting from low frequencies, electric oscillations are the first encountered, the quantum of these being exceedingly small. The element of discontinuity being therefore very small, there is no appreciable deviation from the laws of the electromagnetic theory. Perhaps the smallness of the quantum of electric oscillations may be connected with the nature of the freedom which is possessed by the conductivity electrons of the metals.

The infra-red rays come next; the residual rays of Rubens corresponding to a quantum of the order of one hundredth of a volt.

The luminous rays have a quantum of the order of one volt, which is comparable with the magnitude of a contact

\* In round figures; this numerical value depends on the values adopted for the fundamental constants. Frequently, nowadays, the value 12345 volts is given.

potential difference, i.e. the difference of potential naturally existing between two material surfaces which face each other. This is the source of many difficulties in the investigation of photoelectric phenomena.

The ultra-violet rays begin to have a higher quantum, and the rays in the Lyman region have quanta between 10 and 20 volts.

Between these extreme ultra-violet rays and the X-rays of the longest wave-lengths which have been measured by the ordinary method, there is a gap which extends from  $\lambda = 150 \times 10^{-8}$  cm. to  $\lambda = 12 \times 10^{-8}$  cm., i.e. from  $V = 180$  to  $V = 1000$  volts.

In this region investigation is difficult, because, as will be seen later, absorption is here very pronounced, and because the methods of crystalline analysis are no longer available. Nevertheless, indirect measurements have been made and a collection of trustworthy results proves beyond doubt that the extreme ultra-violet rays and the long wave-length X-rays follow each other continuously.

Beyond this region we find the X-ray spectrum extending from  $12 \times 10^{-8}$  cm. to  $10^{-9}$  cm. with quanta between 1000 and more than 100,000 volts. All these radiations correspond to a well-defined atomic region and to phenomena which are intermediate between those of chemistry and those of radioactivity. It may be said, in fact, that the phenomena of cohesion and chemical phenomena correspond to the luminous and ultra-violet rays, and that there is a gradual change to the phenomena of radioactivity whilst passing through the X-ray region.\*

The  $\gamma$  rays of radioactive substances are reached beyond the X-ray spectrum and have quanta which extend from several hundred thousand volts to several million volts, indicating that the energies called into play in these deep parts of the atom are of a very large order of magnitude.

\* These three groups of phenomena correspond in fact to the forces which affect the electrons of the superficial levels, those of the deep levels, and finally those of the nucleus itself.

Finally, it has been suggested, and M. Perrin in particular attributes the origin of radioactivity to this cause, that all space is traversed by ultra penetrating rays which are situated even beyond the  $\gamma$  rays.

Further, it should be mentioned here that we have been led, theoretically and experimentally, to associate with an undulatory radiation a property which at first sight would appear to belong to a corpuscular radiation. This is the existence of a momentum, a vector which is connected with the pressure of the radiation. A body is subjected to a thrust when a beam of light is incident upon it, and mechanical effects result which have been experimentally demonstrated by Poynting.

Certain facts have even led to the belief \* that the vibratory energy, instead of being uniformly spread over the wave front, is condensed at certain points in a way that recalls the localisation of energy which characterises a projectile in motion. If this be combined with the existence of an inertia for the energy, it will be seen how we get back to the corpuscular theory of radiation.

**3. Corpusecular radiations.**—The study of the rays emitted by radioactive substances, and the analysis of the electric discharge through rarefied gases, led to the discovery of radiations of a nature entirely different from the periodic radiations previously known.

In particular, the cathode rays and the  $\beta$ -rays are composed of moving electrons, for which also a quantum, equal to their kinetic energy, may be defined by writing

$$h\nu = \frac{1}{2}mv^2$$

if the velocity is small compared with that of light, or

$$h\nu = m_0c^2 \left( \frac{1}{\sqrt{1 - \beta^2}} - 1 \right)$$

when  $\beta = \frac{v}{c}$  is comparable with unity.

A little higher up we have defined a quantum for periodic

\* See remarks, p. 185.



vibrations, representing an energy independent of the intensity of the rays; we now attribute to the corpuscles possessed of kinetic energy a quantum equal to this kinetic energy. If this quantum be divided by Planck's constant a frequency is obtained. It will be seen later that this frequency is that of the absorption discontinuity which the corpuscle of quantum  $h\nu$  can just excite. Thus the consideration of the quantum introduces a kind of bond between undulatory and corpuscular radiations; it also expresses the quantity which remains constant when, in contact with matter, one of these radiations is transformed into the other.

**4. Reaction of matter to radiation.**—It is found that when corpuscular rays are incident on matter they give rise to vibratory radiations and vice versa. This transformation obeys a simple law which, in a large number of cases which will be studied in the course of this book, can be expressed as the conservation, or rather, the transference of the quantum. A projectile of kinetic energy  $\frac{1}{2}mv^2 = h\nu$ , when it is suddenly stopped by matter, gives rise to periodic rays of frequency  $\nu$ , and a monochromatic radiation of frequency  $\nu$  detaches corpuscles from a substance on which it is incident, and communicates to them an initial kinetic energy exactly proportional to its frequency and equal to  $h\nu$ .

The following are typical examples of this transformation:—

An evacuated tube is provided with two electrodes between which a potential difference of  $V$  volts is maintained; by heating a filament on the cathode, electrons are produced which are accelerated in the electrostatic field, becoming cathode rays, and possessing when they strike the anticathode an energy  $eV$ . Under these conditions the anticathode emits X-rays, and in the spectrum of the latter it is found that the shortest wave-length emitted corresponds to a maximum frequency  $\nu_{max}$  defined by

$$h\nu_{max} = eV.$$

Conversely, if a substance is exposed to X-rays of this

frequency, corpuscles are emitted similar to the cathode rays of the tube, and possessing an initial kinetic energy equal to  $h\nu$ . (It is advisable to speak of the *initial* kinetic energy because, as we shall see, this preciseness has some importance: if, however, the atomic weight of the substance irradiated is low, the correspondence is very nearly complete).

Thus the quantum is conserved throughout the transformations of the radiations; this example clearly demonstrates that the cathode corpuscles of a given velocity have something in them which permits the definition of a period and that the undulatory X-rays carry, in an indivisible manner, something which reappears under the form of the energy of a single corpuscle.

**5. Secondary or fluorescent rays.**—When a radiation is incident on a certain quantity of matter, for example, on a thin layer of a given substance, it produces a series of characteristic phenomena.

To fix our ideas, let us suppose that the incident radiation has a quantum  $h\nu$ , and possesses, before striking the substance, an intensity  $I_0$ . Part of the incident radiation simply passes through the screen and on emerging it has an intensity  $I_x$  which is generally related to  $I_0$  by the formula

$$I_x = I_0 e^{-\mu x}.$$

This relation indicates that equal thicknesses of matter exercise the same effect on the radiation, whatever the previous reduction of intensity to which it has been subject, and it defines a coefficient of absorption which has the value of the constant  $\mu$ .

Simultaneously, a certain quantity of the primary radiation is diffused in all directions without change of nature, but there may be, in addition, a production of radiation of a new type. This is what is often called fluorescence, and the rays are called secondary rays. The secondary rays may be of the same nature as the incident rays, undulatory like them, for example, with a change of frequency; this

phenomenon is well known in the case of luminous rays. They may also be of quite a different nature from the incident rays. Ultra-violet rays, for example, provoke the emission of electrified corpuscles by the mechanism known under the name of the photoelectric effect, and these corpuscles may be called the secondary  $\beta$ -rays of the ultra-violet rays.

The energy of the different secondary rays is derived from that of the incident rays (unless it is supposed that the latter give rise to a liberation of atomic energy at the expense of the irradiated substance).

The essential feature of the laws which govern these transformations consists in there being a direct relation between *the quantum of the incident rays, the quantum of the secondary rays, and certain quanta characteristic of each element radiated.*

The phenomenon of the excitation of secondary rays, both periodic and kinetic, is appreciable with luminous rays, more marked with ultra-violet rays, and as the frequency increases manifests itself as a perfectly general property of radiation and matter.

The further we advance into the X-ray region the more clearly is the secondary reaction of the radiated matter characteristic of the elements which constitute it. The secondary rays afford a means of obtaining a spectral atomic analysis which permits the immediate recognition of the radiated substance. Beyond a certain frequency, the light brings out the chemical nature of the substance on which it is incident and yields an analysis by fluorescence.

This applies to an incident radiation whether it be periodic or corpuscular, provided that its quantum is sufficiently large. It appears that up to a certain point the laws of radiation can be enunciated in terms of the quantum without consideration of the kinetic or periodic nature of the rays.

The recent experiments of Compton (p. 48) and Wilson (p. 176) have further emphasised and made more distinct the importance of the law of quanta, which will probably involve an essential modification of our present conceptions.

**6. Ionisation and resonance potentials.**—It has been seen that to take an electron from an interior ring to infinity an amount of energy must be expended which is equivalent to the quantum of the absorption discontinuity concerned. This quantum corresponds to the ionisation potential which is defined as follows: the exterior electrons of a gas (of a monatomic gas, for example) are characterised by a work of extraction  $W$ ; to detach them completely, i.e. to produce ionisation, it is necessary to bombard the atom either by corpuscles such that their quantum  $eV$  is at least equal to  $W$ , or by periodic radiations of frequency not less than  $\nu = \frac{W}{h}$ :  $V$  is then called the ionisation potential of the gas.

When the atom again becomes neutral by recombination, it regains its electron and emits luminous rays according to Bohr's theory. These phenomena to-day constitute an important chapter in the excitation of luminous spectra.

It has been experimentally observed that it is possible to excite luminous rays, without provoking gaseous conductivity, by means of electrons having a kinetic energy inferior to that which corresponds to the ionisation potential. This can be explained easily if it is assumed that the incident energy has been employed in removing an electron from the peripheral ring of a normal atom to one of the virtual levels which exist round the atom but which are not, in general, provided with corpuscles. The electron, not being completely detached from the atom, ionisation is not produced, but when it returns to its original position this electron is capable of emitting a radiation of a definite frequency (again according to Bohr's theory). If  $W$  is the work of complete extraction, then  $W_1$ , which is less than  $W$ , will be, for example, the work necessitated by the removal of the electron to its second level; the radiation emitted will have a frequency  $\nu = \frac{W_1}{h}$  and the potential required to obtain an electron capable of exciting this phenomenon will be  $V_1 = \frac{W_1}{e}$ :  $V_1$  is called the resonance potential.

It is obvious that if the electron be on its second orbit it can be removed to a third, farther from the centre of the atom, or even to infinity, if a second exciting corpuscle strike the atom with a suitable energy. Thus ionisation can be produced by successive steps; in other words, a large quantum can be made up by the addition of several small ones.

This type of phenomenon appears to occur in the luminous region but to be absent when X-rays are concerned. It corresponds to line-absorption (Fraunhofer's lines), a fundamental fact in luminous optics, the absence of which for high frequencies is remarkable.

It is probable that the explanation of this divergence is to be found in considerations of temperature. The luminous rays present in the spectrum of a black body at the temperature at which it is studied are in some way in thermal equilibrium under the conditions of production, whilst the radiations of high frequency are only produced in appreciable intensity at temperatures which are very much higher.

#### BIBLIOGRAPHY

1. N. BOHR, *Phil. Mag.*, 1915, 1, p. 332, and 1915, 2, p. 394.
2. J. H. JEANS, *Report on radiation and the quantum theory*. (Publications of the London Physical Society.)
3. SOMMERFELD, *Atombau und Spektrallinien*.
4. E. BAUER, *Théorie de Bohr*. Conférence de la Société de Chimie-Physique.
5. L. BRILLOUIN, *La Théorie des quanta*. Conférence-Rapports sur la Physique.
6. H. G. J. MOSELEY, *Phil. Mag.*, December, 1913, p. 1020, and April, 1914, p. 703.
7. A. LEPAPE, *La discontinuité et l'unité de la matière*. Bulletin de la Société Chimique de France, 4<sup>e</sup> Série, XXXI, Janvier, 1922, p. 1.
8. *Compte rendu du 3<sup>e</sup> Conseil de Physique Solvay*, Brussels, 1921 (Paris, Gauthier-Villars).

## CHAPTER II

### THE SCATTERING OF X-RAYS BY MATTER

ALL the progress realised in X-ray physics in recent years is the consequence of the phenomena of diffraction which these rays experience when they pass through crystalline media, and this action itself is due to the scattering without change of wave-length to which the rays are subject when they strike atoms.

The electromagnetic theory considers the diffusion of light by matter from the following point of view. The electromagnetic field of the wave acts on the electrons of the atoms and communicates to them forced vibrations of the same period and in the same phase as the incident radiation, and these vibrating electrons thus become small oscillators, which act as new sources of radiation.

Before investigating the consequences of such a mechanism in greater detail, we shall briefly recall the principal features of the diffraction of X-rays by crystals. Indeed, this question can be treated by regarding the illuminated atoms simply as centres of diffraction, which are the more active the more electrons they contain, i.e. the greater the atomic mass of the substance.

**1. Diffraction of X-rays by crystals.**—Let us imagine a beam of monochromatic X-rays incident on a material medium and let us adopt the language of the classical electromagnetic theory. In the portion of the matter radiated there will be a certain number of atoms, the electrons of which, entering into forced vibration, will become new sources of radiation of the same frequency as the incident rays. At a distant point, P, the vibrations proceeding from all these atoms must be compounded, account being taken

of the phase differences, and an interference field will result just as in the case of ordinary light; thus a classical diffraction problem is presented.

The results will take a simple form if the distribution of the atoms in the radiated matter is symmetrical. It is well known that in crystallised bodies the matter is arranged in a regular manner with respect to a system of three axes, forming a three-dimensional lattice, according to Bravais' fundamental conception. It may be assumed, for example, that the atoms are placed at the points of the lattice.

Soon after X-rays were discovered crystals were exposed to a beam of the new radiation to find whether it was capable of being doubly refracted and polarised like ordinary light, but nothing could be observed except a simple decrease in intensity of the beam, the direction of which did not appear to be changed at all. It was because the sources of X-rays employed were too weak, and probably also because the investigators were not sufficiently patient, that the fundamental phenomena discovered more than fifteen years afterwards by Laue, Friedrich, and Knipping were not then observed.

In 1912 these three physicists carried out, at Munich, experiments which completely changed X-ray physics and which were the starting-point of all the questions we shall study. If, as Henri Poincaré said, the value of a discovery must be measured by the fruitfulness of its consequences, the work of Laue and his collaborators must count amongst the most important of modern physics.

Laue calculated the phenomena of diffraction in a manner copied from that of ordinary optics; but W. L. Bragg showed shortly afterwards that the same results could be obtained in a very direct and instructive manner.

The points of a Bravais lattice can be distributed in a series of parallel equidistant planes which are called reticular planes. In each reticular plane the points are at the corners of a network of parallelograms.

If the attention be fixed at first on the phenomena of diffraction arising from one reticular plane, and then the effects from all the reticular planes which are parallel to the first be added together, we shall have taken account of all the points of the lattice, which act as centres of diffraction. The first part of this problem does not differ from that which is called in optics the diffraction of a crossed network (or a two-dimensional network), and it is known that the results are as follows :—

If a beam of white light falls obliquely on a plane crossed network, part of the beam is transmitted and continues its path ; in a large number of directions there are coloured images forming the diffraction spectra ; but a large part of the incident energy is found in a regularly reflected beam. This is composed of white light because the path difference is zero for all wave-lengths. We shall consider the regularly reflected beam. (If the centres of diffraction, arranged in the plane, were separated by distances very small compared with the wave-length of light the energy diffracted towards the side of incidence would be concentrated more and more in the reflected beam, which alone would exist, as in the limiting case of mirrors.)

Each reticular plane thus gives its reflected ray ; there is a very large number of parallel reticular planes separated by the same distance  $d$  ; what is the condition that all the reflected rays arising from these planes should interfere with path differences corresponding to a whole number of wave-lengths ? It is easily found that this condition is expressed by

$$n\lambda = 2d \sin \theta \quad . \quad . \quad . \quad (10)$$

$\lambda$  being the wave-length,  $n$  a whole number,  $d$  the distance between the planes, and  $\theta$  the complement of the angle of incidence. Thus the ray from one crossed two-dimensional network will be white ; in the case of a pile of such networks it reduces to wave-lengths which satisfy the preceding relation.



The Bravais lattice may be resolved into systems of reticular planes in an infinite variety of ways, but for some of these planes the density of the points is particularly great; these are the cleavage faces of the crystal. It is easily understood that the most dense planes act the most energetically and that the principal phenomena can be deduced by taking these planes only into consideration.

From our point of view then, the crystalline medium behaves as an assemblage of mirrors at various angles to each other and parallel to the most important faces of the crystalline form. Each of these mirrors, however, is characterised by a certain distance  $d$  (different in general from that which is characteristic of the other mirrors), and it will only reflect rays, the wave-lengths of which satisfy the equation

$$n\lambda = 2d \sin \theta.$$

A circular pencil of complex light traversing a crystal will give, therefore, a certain number of pencils of rays reflected from the cleavage surfaces of the crystal. Each of these pencils conforms to the relation (10), and will correspond to a family of wave-lengths defined by this equation.

We shall not dwell further on this subject, which is now well known. As examples, Figs. 1 and 2 of Plate 1 show crystalline diagrams obtained by Laue's method.

**2. Determination of the absolute value of the reticular distances of crystals and of the wave-lengths of X-rays.**—The relation (10)

$$n\lambda = 2d \sin \theta,$$

shows that if  $\theta$  be measured  $\lambda$  is known in terms of  $d$ . Thus the wave-length of the rays can be calculated if the distance between the reticular planes of a crystal be known; this corresponds to the grating constant in ordinary optics. The problem of determining  $d$  was attacked by Sir W. H. Bragg and his son.

This same relation (10) also shows that if a complex beam

of light falls on a crystalline face characterised by a particular value of  $d$ , the different wave-lengths contained in the incident beam will be dispersed in directions corresponding to definite values of  $\theta$ . Confining our attention to the first order spectrum ( $n = 1$ ), an angle of selective reflection  $\theta$  will correspond to each wave-length; the spectra of higher orders of the same wave-length will correspond to the angles of which the sines are equal to twice, three times, etc., the sine of the angle of the first order.

The structure of a crystal may be studied, for example, by allowing monochromatic light of wave-length  $\lambda$  to fall on the different faces of the crystal and observing the series of selective angles corresponding to the spectra of various orders for each face.

The details of the very delicate arrangements by means of which W. H. and W. L. Bragg have been able to carry out the study of crystal structure will be found in their book, *X-Rays and Crystal Structure*. In addition, a special monograph\* will be devoted to the progress which X-rays have made in crystallography. The aim of the following is only to give an idea of the procedure in this type of calculation and to give an account of the results so far as they specially concern X-rays.

To some extent the arguments advanced by the Braggs rest on a hypothetical basis, but we shall see that the results at which they have arrived appear to be quite justified by conclusions drawn from totally different considerations.

The total mass in a given volume of a crystal being known, it is necessary to know what quantity of substance must be assigned to each point of the lattice in order to ascertain the dimensions of its reticular structure. This can be determined from the study of the spectra reflected from the principal crystalline faces.

Let the most simple class of cubic crystals be considered, for example, the chlorides of potassium and

\* *La Structure des cristaux*. C. Mauguin. In the series *Conférence Rapports de documentation sur la Physique* published by La Société Française de Physique.

sodium. There are several kinds of cubic networks; the simple cube, the face-centred cube, the centred cube; these are three distinct types of the tesseral system (Fig. 2).

In the case of a simple cube, three groups of faces can be visualised; the cubic faces (100), normal to the quaternary axes; the octahedral faces (111), perpendicular to the ternary axes; and the faces of the dodecahedron (110), perpendicular to the binary axes. If  $a$  is the side of the

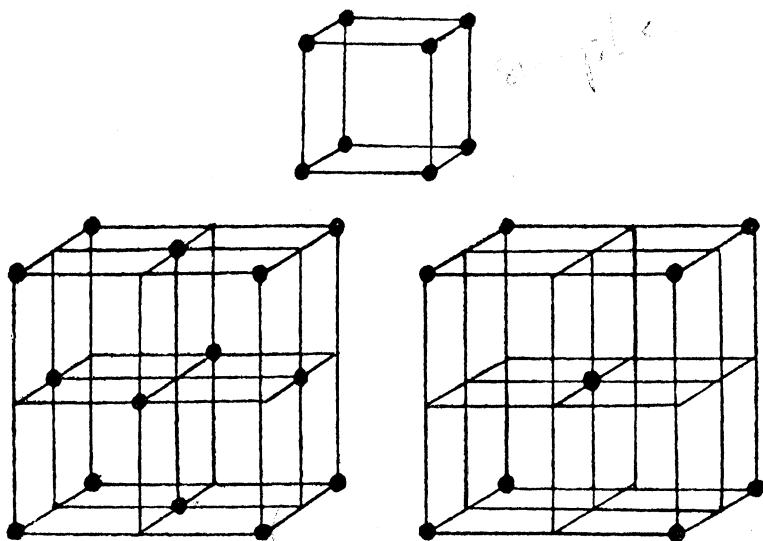


FIG. 2.

cube, the distances between the reticular planes parallel to these faces are

$$d_{100} = a; \quad d_{110} = \frac{a}{\sqrt{2}}; \quad d_{111} = \frac{a}{\sqrt{3}}.$$

If all the points of the simple cubic system act as identical centres of diffraction the reflections from the faces parallel to (100), (110), (111), will give rise to spectra in which the dispersion will be inversely proportional to  $a$ ,  $\frac{a}{\sqrt{2}}$ ,  $\frac{a}{\sqrt{3}}$ .

Bragg has studied the diffraction spectra of a definite

wave-length (the  $K\alpha$  line of palladium, which is easily produced) with sodium and potassium chlorides, and has measured the angles  $\theta$  given by  $\sin \theta = \frac{n\lambda}{2d}$ , for different faces of the cube.

To do this a goniometer is employed, which allows the crystalline faces to be presented to the incident rays at any desired angle, and the reflected radiations are received in an ionisation chamber by means of which their intensity is measured. In this way the spectra of the various orders reflected from each face are found as predicted by the theory, and their relative importance can be compared.

In the case of potassium chloride, the values of  $d$  thus determined for the faces (100), (110), (111), agreed with the values given above. The crystal behaved as though all the points of the simple cubic lattice carried equivalent centres of diffraction.

If the structure of sodium chloride is analogous to that of potassium chloride the lattice of the former substance will only differ from that of the latter by having a different value of  $a$ , and, except for this, exactly the same phenomena should be exhibited by both salts. On the contrary, the experimental results are quite different in the two cases; whilst the intensity of the spectra reflected from all the faces of potassium chloride decreases rapidly as the order increases, the first order spectrum from the (111) face of rock salt is very faint, the second order is strong, the third order weak, the fourth strong, and so on. If only the strong spectra are considered the same simple cubic structure can be assigned to NaCl as to KCl.

On the other hand, if only the first order spectra from all the faces are taken, a face-centred cubic crystal is indicated.

In fact the different types of cubic structure are characterised by the following reticular distances:—

Face.	Centred cube.	Face-centred cube.
(100)	$a$	$a$
(110)	$a\sqrt{2}$	$a/\sqrt{2}$
(111)	$a/\sqrt{3}$	$2a/\sqrt{3}$

The above results can be explained with the help of a few simple hypotheses :—

(1) The simple cube lattice is considered.

(2) Separate atoms are at the points of the lattice, not molecules of NaCl or KCl.

(3) Along the axes and along lines parallel to them there are alternately atoms of metal and metalloid, so that if the system of points with the same chemical element is considered, a face-centred cubic lattice is obtained.

(4) The atoms which act as diffracting points diffract the more energetically the greater their atomic mass.

In connection with these four hypotheses it is necessary to make the following note :—

Let us consider an ordinary grating, such as is used in optics. If it had half the number of lines per centimetre the separation of the spectra of various orders would be reduced by half. But this grating can be supposed to be composed of two intersecting gratings the lines of which are twice as far apart ; this can be done by considering separately the even-numbered and the odd-numbered lines. The effect of the latter, for example, is to destroy, by interference, half the spectra which would be produced by the former if they only were effective. If the odd-numbered lines were less well formed, they would only weaken one spectrum out of two instead of destroying it.

A series of spectra of different orders, in which the spectra are alternately weak and strong, may be considered, therefore, as being produced by a grating, the alternate lines of which are unequally effective.

In a lattice such as that postulated above (Fig. 3), the (100) planes and the (110) planes are all identical and each contains a mixture of atoms of metal and metalloid, but the

(III) planes, which pass through the diagonals of the faces, contain alternately atoms of metal and metalloid.

In the case of potassium chloride, as the chlorine and the potassium have nearly the same atomic mass, they are equally effective from the point of view of diffracting power. All the planes will be equivalent, and the phenomena will only depend on the general lattice which is that of a simple cube. This is not so, however, with sodium chloride, where the metal has an atomic weight appreciably less than that of the metalloid, and therefore the spectra will present

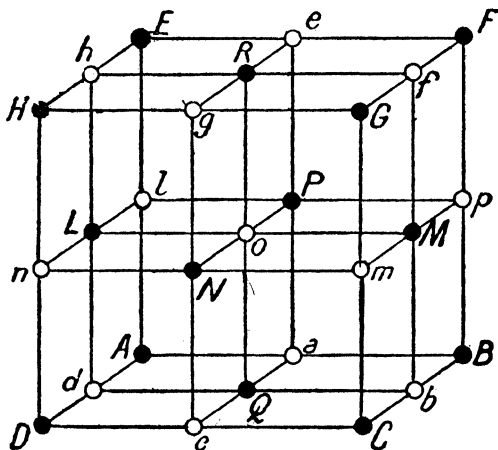


FIG. 3.

alternate intensities which correspond to the unequal diffracting powers of the chlorine planes and the sodium planes.

W. H. and W. L. Bragg have pursued the study of other more complex crystals by analogous reasonings, and have arrived at results which are very interesting but outside the scope of this book. It remains to show how the preceding considerations lead to the determination in absolute value of the wave-length of X-rays.

For this it is sufficient to know the absolute value of the distance between the reticular planes parallel to a system of reflecting faces; for example, the distance between the (100) faces of rock salt.

In the preceding lattice it is easily seen that half a molecule of sodium chloride, i.e. a mass equal to half the molecular mass of this salt, must be associated with each elementary cube.

If  $M$  is the molecular mass of rock salt with respect to hydrogen and  $m_0$  the absolute mass of the atom of hydrogen, then the mass of an elementary cube will be  $\frac{1}{2}Mm_0$ . This mass is also equal to  $\rho d^3$ , where  $\rho$  is the density of the crystal and  $d$  is the side of the cube. Thus

$$d = \sqrt[3]{\frac{Mm_0}{2\rho}},$$

and  $d$  can therefore be evaluated in terms of the density of the crystal and of  $m_0$ , which itself can be calculated by means of Avogadro's number.

In this way, Bragg found that the distance  $d$  between the reticular planes corresponding to the cubic faces (100) of rock salt was

$$d = 2.8 \times 10^{-8} \text{ cm.}$$

Actually, almost all the data relative to rock salt have been calculated using Moseley's value of this constant, namely,

$$d = 2.814 \times 10^{-8} \text{ cm.}$$

The preceding calculation is not quite rigorous and is clearly open to several objections on this account, especially in the case of rock salt, specimens of which are far from having a uniform density. A redetermination of  $d$  has been made for calcite which does not reflect so strongly as rock salt but which is found in much more regular crystals. The distance between the (100) faces of this substance has been found to be \*

$$d = 3.0283 \times 10^{-8} \text{ cm.,}$$

whilst the value calculated from the above value of  $d$  for rock salt † should be  $3.029 \times 10^{-8} \text{ cm.}$  It is seen,

\* See p. 148.

† By the relation  $d \sin \theta = d' \sin \theta'$ .

therefore, that in spite of the objections there is very good agreement.

The values of the reticular distances of some crystals are given in Table III.

TABLE III \*  
(THE DATA HAVE BEEN REDUCED TO VALUES AT 18° C.)

Crystal.	Reflecting Face.	$d$ 10 <sup>-8</sup> cm.	Authors.	Wave-Lengths used Ångström Units.
NaCl	100	2·814	H. G. Moseley, <i>Phil. Mag.</i> , 1913, 26, p. 1024.	Pd $a_1 = 0·5872$ $a_2 = 0·5828$ W. L series
KCl	100	3·136	E. Wagner, <i>Ann. d. Phys.</i> , 1916, 49, p. 625.	
CaCO <sub>3</sub>	100	3·028	W. S. Gorton, <i>Phys. Rev.</i> , 1916, 7, p. 203.	
—	100	3·0279	A. H. Compton, <i>Phys. Rev.</i> , 1916, 7, p. 646.	Cu $(a_1)_2 = 3·078$ Ag $a_1 = 4·146$ Pt $a = 1·316$ $\beta = 1·121$
CaSO <sub>4</sub>	010	7·621	E. Friman, <i>Diss. Lund.</i> , 1916.	
K <sub>4</sub> Fe(CN) <sub>6</sub>	100	8·454†	H. G. Moseley, <i>Phil. Mag.</i> , 1913, 26, p. 1024.	
Mica		10·1	M. de Broglie, <i>Four. de</i> <i>Phys.</i> , 1914, 4, p. 26.	Cu $a_1 = 1·537$ $\beta_1 = 1·391$ Ag $a_1 = 4·146$ $\beta_1 = 3·928$
Quartz		4·246	Siegbahn.	
Saccharose	100	10·56	W. Stenström.	
Complex Ag organic salt AgNaC <sub>6</sub> H <sub>8</sub> O <sub>4</sub> S <sub>2</sub> Na <sub>2</sub> C <sub>6</sub> H <sub>8</sub> O <sub>4</sub> S <sub>2</sub> + 10H <sub>2</sub> O		19·0		

*Remarks on the value of  $d$ ; the limitation which it sets in the application of crystalline diffraction.*—It is interesting to compare the figures thus obtained, which refer to the molecular distances in a solid, with those previously found for the limiting thickness of soap bubbles and films of oil on water, and with the molecular diameters which have been obtained in various ways, in particular by means of the kinetic theory of gases. The same order of magnitude, of 10<sup>-8</sup> cm., is also found for the nearness to which two atoms must approach in order to exert on each other intense cohesive forces or to collide.

\* Stenström, *Ann. der Physik*, 1918, XXI, p. 347.

† This value has been redetermined by Siegbahn with greater accuracy; he gives the value 8·408 . 10<sup>-8</sup> cm.



If the value of  $d$  is known for one crystal, that for other crystals can be deduced therefrom by comparing the deviations of the same radiation, using the formula

$$d \sin \theta = d' \sin \theta',$$

$d$  is large for substances which cleave easily (gypsum, mica, etc.), and when this distance has values greater than  $10 \times 10^{-8}$  cm. the cohesion is no longer sufficiently strong to ensure that the substance holds together. It is true that complex molecules, in which a heavy atom, efficacious as a centre of diffraction, would be far removed from other similar atoms, might be used for X-ray purposes, cohesion being assured by a large number of light atoms which are comparatively inactive. This is the case with the silver salt which is placed last in Table II, but hitherto such crystals have not been of practical use. This limit of the reticular distances thus imposes a restriction on the wave-lengths reflected. In the formula  $\lambda = 2d \sin \theta$  the maximum value of  $\lambda$  is equal to  $2d$ . This value cannot be quite attained because then the reflected ray returns along the path of the incident ray, and, in fact, the largest values of  $\lambda$  actually measured by crystalline diffraction are between 12 and  $13 \times 10^{-8}$  cm. (the shortest are of the order of  $0.1 \times 10^{-8}$  cm.).

A. H. Compton,\* Birge,† Ledoux-Lebard and Dauvillier,‡ and Siegbahn,§ have calculated and discussed the most probable value of the constant  $d$ , especially for rock salt and calcite.

Siegbahn evaluated the reticular separation of calcite directly, and concluded that

$$d = (3.0283 \pm 0.002) \cdot 10^{-8} \text{ cm.}$$

Particulars of the values adopted for the constants involved in the estimation of this magnitude will be found on page 149.

The methods actually employed in the measurement of wave-lengths by their angles of selective reflection are capable

\* *Phys. Rev.*, 1918, I, p. 430.

† *Ibid.*, 1919, I, p. 361.

‡ *Comptes Rendus*, 1919, II, pp. 788 and 965.

§ *Phil. Mag.*, 1919, p. 601.

of great accuracy, and the results are finally expressed in terms of a certain assumed value for the  $d$  of the crystal employed. It is desirable that the data should be completely co-ordinated by adopting, for example, the value 3.028 for calcite.

*Confirmations of the values found for wave-lengths.*—Bragg's calculations are partly hypothetical, notably as regards the position of single atoms at the points of the simple cube lattice; the calculation also involves Avogadro's number, the density, and the molecular mass. The wave-lengths thus obtained are to some extent minimum values, since the smallest portions of matter, the atoms,\* are supposed to be concentrated at the points. It may be questioned, therefore, whether Bragg's calculations really give the absolute values of the wave-lengths or only quantities to which they are proportional.

Several confirmations, based on distinct phenomena, are available, which appear to place the validity of the numbers obtained for the wave-lengths beyond doubt. The following may be cited :—

The results of the Bohr-Sommerfeld theory apply from the visible region up to Röntgen rays and thus provide a bridge between X-rays and those of light, the wave-lengths of which are known without ambiguity.

Again, an X-ray tube working under a known difference of potential  $V$  emits a continuous spectrum of radiations definitely limited on the short wave-length side. But it appears certain that the quantum relation applies to this limiting wave-length under the form  $eV = h\nu$ , in which  $eV$  is the energy of the cathode electrons in the tube,  $h$  is Planck's constant, and  $\nu$  is the frequency of the limiting radiation. This frequency  $\nu$  involves the wave-length  $\lambda$ , and the verification of Planck's law requires the value of  $\lambda$  calculated by means of Bragg's theory.

Still another argument is found in the photoelectric

\* More accurately, according to Bragg's theory, the ions Cl and Na, for example, occupy the points of the lattice.

effects produced by Röntgen rays (see Chap. VI). This phenomenon consists in the expulsion of electrons from substances exposed to the rays, and the kinetic energy of these electrons satisfies Planck's relation, applied to Bohr's atom model, if the values of the wave-lengths obtained by crystal analysis are employed.

In these two last examples, it may be said that if Planck's law be admitted then the wave-lengths can be ascertained by measuring a potential difference or a magnetic field.

Finally, and this will eventually afford the decisive proof, the gap between the extreme ultra-violet and the X-rays is continually decreasing, the unknown region now only extending from the radiation  $\lambda = 144.3 \times 10^{-8}$  cm. measured by Millikan, on the ultra-violet side, to the X-ray wave-length  $\lambda = 12.35 \times 10^{-8}$  cm. obtained by Siegbahn. When the junction is accomplished there will be a gradual transition from the measurement of optical wave-lengths to that of X-ray wave-lengths, and the absolute value of the latter will receive the definite confirmation concerning which there is even now but little doubt.

### 3. More complete theory of the scattering of X-rays.

**Influence of thermal agitation.**—Laue's theory assumes that only the points of the crystalline lattice act as diffracting centres. Actually, the problem is not so simple since the atoms are not immobile but are in irregular motion due to thermal agitation, and, moreover, each of them contains a large number of electrons which themselves present various configurations and motions.

Quite early on the effect of the thermal agitation was very happily investigated by Debye [4]. What might have been surprising was to find that, as de Broglie [5] had shown, the good definition and the general appearance of the interference spots do not appear to be modified appreciably as the temperature is raised from that of liquid air to that of red heat.

To explain the action of temperature, Debye's theory leads to the introduction in the expression for the intensity

of a ray diffracted in a direction making an angle  $\delta$  with the direction of the incident ray, of the factor

$$e^{-\frac{4\pi^2 k T}{f \lambda^2} 2(1 - \cos \delta)}$$

where  $T$  is the absolute temperature,  $k$  is Boltzmann's constant, and  $f$  a magnitude measuring the elastic force which retains the atoms in their position of equilibrium. This results in the sharpness of the interference maxima being undiminished, but also results in their intensity and that of the continuous background from which they stand out depending on the temperature in an exponential manner.

The intensity of an interference maximum diminishes as the deviation  $\delta$  increases, as the temperature rises, and as the wave-length decreases. Laue and van den Lingen, and especially Bragg [2], have shown by remarkable experiments that Debye's theory appears to be quantitatively correct. Debye has discussed this question in a slightly different way in another paper.\* The factor  $f$  which is involved in the preceding formula is related to Lindemann's "natural periods" and to the deviations from Dulong and Petit's law of specific heats.

Jauncey [23] examined experimentally the intensity of the scattered radiation and found that Debye's prediction that the scattering by amorphous substances should be different from the scattering by crystals was not verified. The same author [24] also investigated the effect of change of temperature on the scattering. Rock salt showed a marked temperature effect, but it was considerably less than that calculated from Debye's theory, while with calcite there was practically no change in the intensity of the scattered radiation when the temperature was raised from 17° C. to 292° C.

Backhurst [25] has examined the thermal effect for the radiation regularly reflected from crystals of aluminium, diamond, carborundum, graphite, and sapphire. Variations

\* *Annalen der Physik*, 1914.

in the reflected intensity were observed with all these crystals but the diamond, which showed no appreciable change with temperature up to 880° C. The variations were not in accord with Debye's theory.

The problem has also been theoretically investigated by L. Brillouin [26] who intimates that the scattering by crystals may be unaffected by temperature.

In addition, the temperature may have another effect, namely, that of disturbing the exterior levels of the atoms by removing their electrons ; this will be referred to later.

Finally, the crystal expands, and its reticular distances vary with the temperature according to the laws which characterise its anisotropy.

**4. Influence of the number and disposition of the electrons in the atom.**—Relying solely on the electromagnetic theory, Sir Joseph Thomson in his classical treatment of the diffusion of X-rays showed that a substance containing  $N$  electrons per unit volume has a scattering power proportional to

$$\frac{8\pi}{3} \frac{Ne^4}{m^2}.$$

This expression is *independent* of the wave-length, and Barkla deduced from it, by experimental measurements, that the number of electrons contained in each atom is of the order of half the atomic weight.

In Thomson's calculation the action of the wave on each electron is considered separately, and it is found that the *intensity* of the scattered radiation due to the collection of  $N$  electrons is proportional to  $N$ . This assumes that the phases of the oscillations of the electrons are not related to each other. If the vibrations were all in phase (for example, in the case where the distance between the electrons is small compared with the wave-length) the resultant *amplitude* would have to be considered proportional to  $N$ .

If it is desired, however, to investigate thoroughly the phenomenon of scattering by atoms it is necessary to take

account of the arrangement of the electrons in the atom, as well as the relative dimensions of their orbits and the incident wave-lengths.

Debye [6] has examined in detail the case of a radiation scattered by a group of atoms arranged irregularly as in amorphous bodies, by assuming that the velocities of the electrons are so small that they can be considered stationary during the period of the incident wave, and by imagining that the corpuscles are situated on a circle of radius  $a$  in the atom. It can be shown in this way that the nature of the phenomenon must depend on the value of  $\frac{\lambda}{a}$ .

If  $\frac{\lambda}{a}$  is big, the energy scattered is proportional to the *square* of the number of electrons, and is distributed symmetrically with respect to the direction of incidence.

If  $\frac{\lambda}{a}$  is small Thomson's formula results, and the energy is directly proportional to the number of electrons, but periodic variations of the diffracted intensity must be expected, the period being a function of the angle between the incident and the diffracted rays. These variations will be observed as bright and dark rings with their centres on the direction of incidence.

At first Debye thought he found a verification of this theory in the halos which are observed round beams of X-rays which have passed through metallic films, through powdered crystals, or through certain substances which are usually considered amorphous. Actually, however, these are caused in quite a different way, simply arising from the presence of a large number of very small crystals oriented in all directions.

These phenomena, which depend on the arrangement of the atoms in the substance and not on that of the electrons in the atoms, will be considered elsewhere (p. 153).

**5. The coefficient of reflection of X-rays from crystalline faces.**—In the diffraction of X-rays by crystals, not

only the positions of the diffraction maxima have to be considered; many other problems present themselves. The ratio of the reflected intensities to the incident intensities under different conditions must also be investigated.

For example, it would be very interesting to know how the coefficient of reflection of a given wave-length varies for different faces; or, using the same face, how it varies with spectra of different orders; or, again, what is the variation of this coefficient with the wave-length using the same face and the same order.

As a layer of crystal of finite thickness is concerned in the reflection of the rays, these will be more or less absorbed in their path, but the problem is complicated by the fact that a perfect crystal, which presents the same lattice throughout the thickness of the active layer, is not always available.

So far as is possible, Darwin [7] and Compton [8] have discussed this question from the theoretical point of view, and have derived an expression for the coefficient of reflection of which W. L. Bragg, James, and Bosanquet [9] have given a simple demonstration. This formula is as follows:—

$$R = \frac{N^2 \lambda^3}{2\mu \sin 2\theta} F^2 \frac{e^4}{m^2 c^4} \frac{1 + \cos^2 2\theta}{2} e^{-\frac{\beta \sin 2\theta}{\lambda^2}}$$

in which  $N$  is the number of electrons per unit volume,  $\mu$  the coefficient of absorption of the rays in the crystal,  $\theta$  the angle of reflection, and  $F$  a function which depends on the angle of diffraction and on the positions of the electrons in the atom. The exponential factor accounts for Debye's thermal effect.

The quantity  $R$  thus defined represents the ratio  $\frac{E\omega}{I}$ , in which  $E$  is the total energy of a given wave-length reflected per second when the crystal rotates with an angular velocity  $\omega$  (in radians per second);  $I$  being the energy which the beam sends in one second through the slit of an ionisation chamber.

It is necessary to have recourse to a definition of this kind because the finite width of the pencils of rays and the imperfections of the crystals permit energy to be reflected not only at a well-defined angle  $\theta$ , but over a small angular distance  $\Delta\theta$ , which may amount to an appreciable fraction of a degree. (On account of the geometrical property described on page 134, this does not prevent very accurate determinations of the angle of selective reflection of extremely fine pencils.)

Bragg and Bosanquet [9] measured experimentally the ratio  $\frac{E\omega}{I}$  for the (100) face of rock salt and the  $K\alpha$  doublet of rhodium, and found

$$\frac{E\omega}{I} = 0.000612.$$

The effective angular distance being of the order of a degree, this result must be multiplied by 60 to obtain the true value of the coefficient of reflection (ratio of the reflected energy to the transmitted energy). This coefficient thus becomes 0.04.

Table IV shows the values of the reflecting power for other faces of rock salt expressed as percentages of the value for the (100) face. In this table, moreover, the reflected intensities are approximately proportional to  $\frac{I}{\sin^2 \theta}$ . It is not easy to explain simply this law to which W. L. Bragg has already called attention, but it must not be forgotten that in the theoretical expression for  $R$ ,  $F$  is also a function of  $\theta$ .

Compton [10] and Bergen Davis [11] have also measured the reflection coefficients for rock salt and calcite.

The determinations made in the laboratory of Bergen Davis were carried out for a series of radiations reflected at angles between  $3^\circ$  and  $9^\circ$  from a calcite crystal. They lead to values of the reflection coefficient which decrease as the wave-length increases, and which are much greater than those previously obtained; calcite, however, reflects



four times less strongly than rock salt. There is here a disagreement which appears to call for further investigation.

The measurements have recently been repeated by Wagner [17] and by Bergen Davis [18]. They give fresh information without definitely deciding the question.

TABLE IV \*

Reflecting Plane.	Intensity.	Reflecting Plane.	Intensity.
100	100	111	9'00
200	19'90	222	33'1
300	4'87	333	0'58
400	0'79	444	2'82
500	0'116	555	0'137
110	50'4	311	1'17
220	6'10	622	2'69
330	0'71		
		331	0'81
		511	0'61
		711	0'302

TABLE IVA †

REFLECTION COEFFICIENTS

Authors.	$\lambda$ in Å.	$E_{\omega} \cdot 10^5$ .	
		Calcite.	Rock Salt.
Davis and Hempel . . . . .	0'37	—	—
	0'58	ca 8'9	—
	0'79	—	—
Bragg . . . . .	0'615	—	54'1
	1'39	7'6	—
	1'54	7'95	26'8
Wagner and Kuhlenkampff	1'75	7'82	—
	1'93	7'51	18'7

*Electronic connection between the atoms in the crystal.*—The comparison with experiment of the theoretical expression for  $R$  has been undertaken by W. L. Bragg and his collaborators, and may be of great importance because it allows the function  $F$  to be determined. The knowledge of this

\* W. L. Bragg, James, and Bosanquet, *Phil. Mag.*, March, 1921.

† Wagner and Kuhlenkampff, *Phys. Zeits.*, 1922, p. 503.

yields valuable information on the number and arrangement of the electrons in the atoms of the reflecting crystal.

Debye and Scherrer have also carried out similar investigations, and in particular have obtained very interesting results on the constitution of lithium fluoride [12].

Following Debye, we shall represent the scattered amplitude due to the atom of lithium by (Li), that due to the fluorine atom by (F). Bragg's researches have led to the following structure being assigned to the lithium fluoride family (sodium chloride, potassium chloride, sodium fluoride, etc.): the atoms of each of the constituents are placed alternately on the rows of the cubic lattice, each atom of one kind being preceded and followed by an atom of the other kind. Laue's theory shows that, under these conditions, only the reticular planes of which the indices  $h_1, h_2, h_3$ , are either all odd or all even can reflect. The reticular planes, the indices of which are all even, give a reflected intensity proportional to  $[(Li) + (F)]^2$ . The reflected intensity when the indices are all odd is  $[(Li) - (F)]^2$ .

Debye and Scherrer worked with the method described in section 10 of Chapter V, using powdered lithium fluoride. The phenomenon observed consisted in the production of concentric rings each of which corresponded to a reticular plane. The value of the ratio

$$\frac{[(Li) + (F)]^2}{[(Li) - (F)]^2}$$

can be calculated from the results. Near the prolongation of the direction of incidence Debye and Scherrer found

$$\frac{(Li) + (F)}{(F) - (Li)} = 1.5.$$

If Bragg's law that the scattered amplitude is proportional to the number of electrons in the atom is assumed, it is seen that this ratio is verified if (Li) and (F) are assumed to be proportional to 2 and 10 respectively, since  $\frac{12}{8} = 1.5$ . Normally, the fluorine atom possesses nine electrons and the

lithium atom three. It is therefore necessary to assume that the combination of lithium and fluorine involves the transfer of an electron from lithium to fluorine.

This example shows how the investigation of these phenomena is capable of yielding important and interesting information concerning the connection between molecules.

In a recent paper [19], W. L. Bragg, James, and Bosanquet have discussed the conclusions which may be reached in this direction.

*Abnormal absorption.*—When a monochromatic beam falls exactly at the angle of selective reflection on a layer of matter having a perfect crystalline structure, it is absorbed to an abnormally great extent, since the reflected beam, which is also incident on the lattice at the selective angle, is itself reflected towards the interior of the crystal. If the medium has not a perfect crystalline structure this effect will not be produced to the same extent, and W. L. Bragg has investigated this phenomenon experimentally, showing notably that the coefficient of reflection is not the same at a rock salt face produced by good cleavage as at the same face rubbed with emery paper, which partly destroys the perfection of the crystalline lattice; the reflection is more intense in the second case.

The relation between the intensities of reflection for a given wave-length using spectra of different orders has also been investigated by W. L. Bragg who found that the coefficients of reflection for the first five orders were in the ratios

$$100 : 20 : 7 : 3 : 1.$$

Darwin's theory indicated that they should vary as  $\frac{1}{n}$ ; the observed decrease is much more rapid.

Darwin [16] has recently published a general review of this problem of crystalline reflection and the difficulties which appear when it is desired rigorously to evaluate the coefficient of reflection.

**6. Absorption resulting from scattering.**—The energy of

a beam of X-rays incident on a collection of atoms is partially scattered in all directions because of the phenomena of diffusion, and thus the intensity of the beam decreases as the thickness traversed increases. It will be seen later, in Chapter IV, that the strongest cause of the absorption of X-rays, and the mechanism most closely related to the constitution of the atom, consists in what is known as *fluorescent absorption*. We shall consider here only the absorption due to scattering.

When the irradiated atoms form part of a crystalline lattice interference occurs for certain wave-lengths and for certain directions of incidence, giving rise to reflected rays. On the other hand, at the moment of selective reflection the energy of the beam in the prolongation of the direction of incidence is destroyed by interference. This phenomenon has been referred to in the last section in connection with W. L. Bragg's researches. In the case where the atoms are arranged quite irregularly, scattering takes place in all directions, and depends on the atomic number of the irradiated substance as well as on the wave-length.

If  $\sigma$  is the exponential coefficient of absorption, the quantity which is normally measured is  $\frac{\sigma}{\rho}$ , where  $\rho$  is the density. Unfortunately the study of this coefficient is insufficiently advanced for the enunciation of any laws regarding its variation.

It has been seen above (paragraph 4) that the absorption due to scattering should depend theoretically either on the number of electrons in the atom or on the square of this number, according to the magnitude of the ratio of the wave-length to the atomic dimensions. Thomson's classical formula corresponds to small values of this ratio.

In fact, though it has not been possible hitherto to do anything more than make rather indirect determinations of  $\frac{\sigma}{\rho}$  the experimental observations, among which should be noted those of Barkla, Barkla and Miss Dunlop, Crowther,

Holthusen, Dessauer, Hull and Rice, Soddy, Russell, Ishino [13] and particularly of Hewlett, and Richtmeyer [14], have led to the following conclusions.

For the light elements, with both large and medium wave-lengths, the coefficient  $\frac{\sigma}{\rho}$  is approximately constant and of the order of 0.17 whatever the wave-length and the element (except in the case of hydrogen for which the coefficient is about twice as large). This numerical value is in fairly good agreement with that predicted by the classical electromagnetic theory.

The variation of  $\frac{\sigma}{\rho}$  is more complicated for the heavy elements. Even for wave-lengths of an Ångström unit and above it varies greatly with the frequency, decreasing as the latter increases, and for all elements it assumes *very low* values when the frequency becomes very great. For hard  $\gamma$ -rays  $\frac{\sigma}{\rho}$  should be of the order of 0.05.

Some recent measurements of the coefficient of absorption due to scattering are collected in Table V. It will be seen

TABLE V \*

Elements.	$\frac{\sigma}{\rho}$ Observed.	$\frac{\sigma}{\rho}$ Calculated by Thomson's Formula.
Hydrogen . . . .	0.309	0.3987
Lithium . . . .	0.157	0.1737
Carbon . . . .	0.175	0.2009
Nitrogen . . . .	0.168	0.2008
Oxygen . . . .	0.165	0.2010
Aluminium . . . .	0.173	0.1928
Iron . . . .	0.18	0.1871

that this coefficient has a systematic tendency to be less than its theoretical value.

Further knowledge of this coefficient would be very valuable on account of the theoretical interpretations to

\* C. W. Hewlett, *Phys. Rev.*, March, 1921.

be based on it. It is greatly to be desired that rapid progress should be made in its study.

Compton has explained the rapid decrease of  $\frac{\sigma}{\rho}$  for short wave-lengths by assuming an annular structure\* of the negative charges which constitute the electron [15].

In conclusion, this chapter calls for a last remark. The phenomena of interference and scattering with which it is concerned have been treated with some success on the classical electromagnetic theory, without that introduction of quanta which will be so prominent in the following chapters. The new experiments described in the following paragraph indicate, however, that the classical theory of scattering should only be considered as a first approximation.

**7. Change of wave-length by scattering.**—By examining spectroscopically the radiation scattered at an angle in the neighbourhood of  $90^\circ$  when the X-rays of molybdenum were incident on a graphite radiator, A. H. Compton showed [20] that the wave-lengths were increased, so that, for example, the  $\alpha$  line moved from the wave-length  $0.708 \text{ \AA.}$  to  $0.730 \text{ \AA.}$ , being an increase of  $0.022 \text{ \AA.}$ , or nearly 3 per cent. of the initial wave-length.

This experiment, which followed others which were less exact [21], has been repeated by Ross [22], who employed the photographic method, whereas Compton used the electro-metric method. Ross used a Coolidge tube with a water-cooled molybdenum anticathode, working at 42,000 volts and 25 milliamperes; he employed a fixed crystal of calcite. First an exposure of five minutes was given with the  $\alpha_1$  and  $\alpha_2$  lines directly, and then an exposure of 100 hours when the same radiations were scattered by a block of paraffin wax, the angle of scattering being  $90^\circ$ . The result was that the radiation scattered by the paraffin wax consisted of:—

1. The original lines, undisplaced; and
2. These same lines, much stronger, displaced about  $0.025 \text{ \AA.}$

\* This annulus must have a diameter of the order of one thousand times that which is accepted for the electron ( $10^{-13} \text{ cm.}$ ).

In spite of the narrowness of the slit the lines in the second photograph were very much broadened.

*Theory* (Compton and Debye).—Consider an electron and suppose it, at first, to be free or feebly constrained, and let there be incident on it a radiation of frequency  $\nu$ .

According to the classical theory it should enter into forced vibration with a frequency exactly equal to  $\nu$  and should scatter radiation of this frequency in all directions; this radiation will be polarised if examined at an angle of  $90^\circ$ . The classical theory does not predict a change of frequency.

According to the new ideas of Compton and Debye it is supposed that a double effect results when the radiation

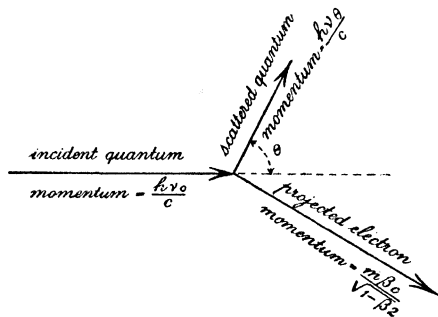


FIG. 4.

of frequency  $\nu_0$  is incident on a scattering electron. Firstly, there is the emission of a scattered radiation at an angle  $\theta$ , the frequency of which is  $\nu_\theta$ , and secondly, a certain recoil of the electron with a velocity  $v = \beta c$  (Fig. 4); the conservation of momentum and the conservation of energy will then give two equations whence  $\nu_\theta$  and  $v$  can be determined. The momentum attributed to the undulatory radiation will be  $\frac{h\nu}{c}$  and its energy  $h\nu$ ; for the electron the corresponding magnitudes will be respectively

$$\frac{m_0\beta c}{\sqrt{1-\beta^2}}$$

and

$$m_0 c^2 \left( \frac{1}{\sqrt{1 - \beta^2}} - 1 \right).$$

Therefore

$$\left( \frac{m_0 \beta c}{\sqrt{1 - \beta^2}} \right)^2 = \left( \frac{h\nu_0}{c} \right)^2 + \left( \frac{h\nu_\theta}{c} \right)^2 - 2 \frac{h\nu_0}{c} \cdot \frac{h\nu_\theta}{c} \cos \theta \quad (11)$$

and

$$h\nu_\theta = h\nu_0 - m_0 c^2 \left( \frac{1}{\sqrt{1 - \beta^2}} - 1 \right) \quad (12)$$

and the expression for the change of wave-length resulting from the scattering at an angle  $\theta$  will be

$$\Delta\lambda = \frac{2h}{m_0 c} \sin^2 \frac{\theta}{2} = 0.0484 \sin^2 \frac{\theta}{2}$$

in Ångström units, which is in good agreement with experiment.

Ross has endeavoured to find a change of wave-length by scattering in the case of visible light by the examination of the structure of the green line of mercury (5461 Å.) with a powerful interferometer. However, he could observe no difference between the direct beam and that scattered by a block of paraffin wax at an angle of  $180^\circ$ , though the theoretical variation under these conditions should have been easily distinguishable.

Jauncey and Wolfers have emphasised the consequences which Compton's phenomenon involves with respect to the calculation of wave-lengths by crystalline diffraction; in particular there should be small differences between the values obtained from spectra of different orders, but the experimental results seem to indicate that Bragg's theory does not cease to apply.

The results of Compton and Ross can be reconciled with the numerous phenomena by which Bragg's theory has been verified, by assuming that, in the scattering of X-rays, only the rays scattered without change of wave-length retain a definite phase relation with the incident rays. The diffraction calculations and the maxima which result therefrom



will therefore be applicable only to these rays and not to that portion of the radiation which has changed its wave-length.

## BIBLIOGRAPHY

1. M. LAUE, W. FRIEDRICH, and P. KNIPPING, *Interferenz-Erscheinungen bei Röntgenstrahlen. Berichte de l'Académie des Sciences Bavaroise*, 8 June, 1912.
2. SIR W. BRAGG and W. L. BRAGG, *X-rays and crystal structure*.
3. W. DUANE, *Data relating to X-ray spectra. Bulletin of the National Research Council Published by the National Academy of Sciences* (Washington).
4. DEBYE, *Über den Einfluss der Warmebewegung auf die interferenz-erscheinungen bei Röntgenstrahlen. Verhandlungen der Deutschen Physikalischen Gesellschaft*, 1913, 15 and 16; and *Ann. der Phys.*, 1915, 43, p. 49.
5. M. DE BROGLIE, *Recherches sur la diffraction des rayons de Röntgen par les milieux cristallins. Comptes Rendus*, 1913; and *Le Radium*, June and August, 1913.
6. DEBYE, *Diffusion des rayons de Röntgen, Ann. der Phys.*, 1915, 46, p. 809.
7. C. G. DARWIN, *Phil. Mag.*, 1914, 1, p. 315.
8. A. H. COMPTON, *Phys. Rev.*, 1916, 1, p. 658, and 1917, 1, p. 29.
9. W. L. BRAGG, R. W. JAMES, and C. H. BOSANQUET, *Phil. Mag.*, 1921, 1, p. 309, and 1921, 2, p. 1.
10. A. H. COMPTON, *Phys. Rev.*, 1917, 2, p. 95.
11. BERGEN DAVIS, *Phys. Rev.*, 1918, 1, p. 433, and 1919, 2, p. 539.
12. DEBYE and SCHERRER, *Phys. Zeits.*, 1918, p. 474.
13. BARKLA and SADLER, *Phil. Mag.*, 1918, 2, p. 550.  
BARKLA and MISS DUNLOP, *Phil. Mag.*, 1916, 1, p. 222.  
CROWTHER, *Proc. Camb. Phil. Soc.*, May, 1911.  
HULL and RICE, *Phys. Rev.*, 1916, 2, p. 326.  
HOLTHUSEN, *Phys. Zeits.*, 1919, p. 5.
14. HEWLETT, *Phys. Rev.*, 1921, 1, p. 228.  
RICHTMEYER, *Phys. Rev.*, 1921, 1, p. 228, and 1921, 2, p. 13.
15. A. H. COMPTON, *Phys. Rev.*, 1919, 2, p. 20.
16. C. G. DARWIN, *Phil. Mag.*, 1922, 43, p. 800.
17. WAGNER, *Ann. der Phys.*, 1922, 13, p. 639.
18. BERGEN DAVIS, *Phil. Mag.*, March, 1923, p. 463.
19. W. L. BRAGG, JAMES, and BOSANQUET, *Phil. Mag.*, 1922, No. 261, p. 433.
20. A. H. COMPTON, *Phys. Rev.*, May, 1923.

21. A. H. COMPTON, *Bull. Nat. Res. Council*, 1922, No. 20, p. 17.
22. ROSS, *Proc. Nat. Acad.*, July, 1923, p. 246.
23. JAUNCEY, *Phys. Rev.*, 1922, 20, p. 405.
24. JAUNCEY, *Phys. Rev.*, 1922, 20, pp. 82 and 421.
25. BACKHURST, *Proc. Roy. Soc.*, 1922, 102, p. 340.
26. L. BRILLOUIN, *Ann. de Physique*, 1922, 17, p. 88.

For an account of certain abnormal phenomena established in some cases of the diffraction of X-rays by crystals, see also the papers of Clark and Duane (*Nat. Acad. Proc.*, April, 1923, p. 226), and McKeehan (*Science Abstracts*, May, 1923, p. 275).

## CHAPTER III

### THE ABSORPTION OF X-RAYS BY MATTER

**1. Coefficients of absorption.**—As with luminous rays, an exponential coefficient of absorption  $\mu$  can be defined for X-rays by the equation

$$I_x = I_0 e^{-\mu x}$$

where  $I_x$  is the intensity of a beam after traversing a thickness  $x$  of the absorbing substance, the initial intensity being  $I_0$ . As a matter of fact, the absorption consists of at least two totally distinct phenomena ; one is the simple scattering of the incident radiation without change of wave-length \* which has been studied in the last chapter, and the other, often called fluorescent absorption, concerns the portion of the energy which the atom, by a mechanism which is completely unknown, transforms into secondary rays of a vibratory or corpuscular nature quite different from the incident rays.

Finally, some of the energy, arising mainly from the very absorbable secondary  $\beta$ -rays, remains in the absorbing substance and appears in the form of heat. Thus the coefficient  $\mu$  can be regarded as the sum of two other coefficients  $\tau$  and  $\sigma$  which refer to fluorescence and scattering respectively.

All these coefficients are atomic properties and do not depend † on the physical or chemical state of the substance used as a screen. The absorption caused by a layer of known thickness of a given element therefore depends only on the number of atoms contained in this layer. Hence the

\* Except as discussed in the last paragraph of Chapter II.

† At least to a first approximation.

quotients  $\frac{\mu}{\rho}$ ,  $\frac{\tau}{\rho}$ ,  $\frac{\sigma}{\rho}$ , of the absorption coefficients for a given element and a given radiation are constants, whatever the physical state of the element. These expressions are often called mass absorption coefficients; they measure, in fact, the absorption by a screen of such a thickness that it contains unit mass per square centimetre.

The coefficient

$$\frac{\mu A}{\rho},$$

in which  $A$  is the absolute mass of an absorbing atom, will be an atomic absorption coefficient, corresponding to a screen which contains one atom per square centimetre.

**2. Absorption corresponding to fluorescence.**—Except for the light elements, the absorption due to scattering is negligible compared with that due to fluorescence. The latter is also much the more important on account of its connection with the energy levels of Bohr's atom. All the experimental results referring to the measurement of the absorption coefficient show that the latter is a function both of the atomic number  $N$  of the absorbing substance and of the wavelength  $\lambda$ . Although the data so far available are not yet sufficiently numerous nor sufficiently accurate to permit the enunciation of an exact and definite law, they satisfy, on the whole, the relation

$$\frac{\tau A}{\rho} = CN^4\lambda^3$$

which is known as Bragg and Peirce's law [I].\*

In this formula,  $C$  remains constant in certain regions and passes abruptly from one value to another at definite values of  $N$  and  $\lambda$ .

Bragg and Peirce's law is represented graphically in three dimensions as a function of two independent variables,

\* As  $A$  is roughly proportional to  $N$  this may also be written  $\frac{\tau}{\rho} = C^1 N^3 \lambda^3$ .

The index of  $\lambda$  has given rise to some discussion. In Bragg's preliminary work this index was stated to be  $5/2$ , but the value 3 appears much more probable to-day.

$N$  and  $\lambda$ , but it can be studied by the examination of sections parallel to the planes of co-ordinates.

For example, if  $N$  be kept constant, a curve showing the variation of  $\frac{\tau}{\rho}$  with  $\lambda$  is obtained. In this way the coefficient of absorption of a given substance can be studied as a function of the wave-length. On the other hand, if  $\lambda$  be kept constant and  $N$  varied, the law governing the absorption of a given radiation by screens composed of different elements results.

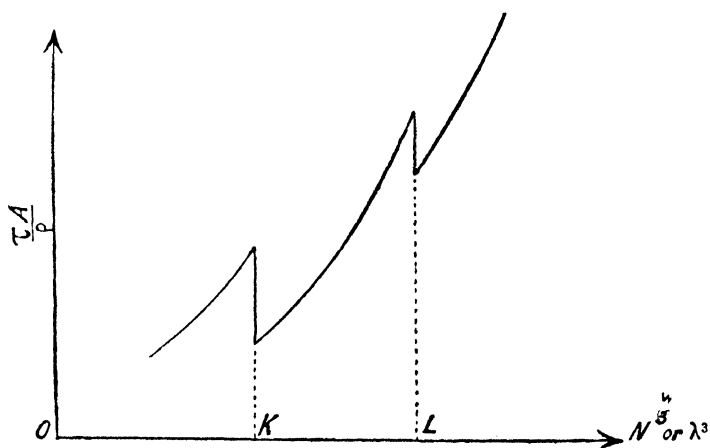


FIG. 5.

The two curves thus obtained will be very similar (the note on the preceding page even indicates that  $\frac{\tau}{\rho}$  is nearly symmetrical in  $N$  and  $\lambda$ ), and to a first approximation will be of the type shown in Fig. 5.

For certain values of  $N$  and  $\lambda$  the absorption coefficient increases abruptly and then again commences to decrease.

If the logarithm of  $\frac{\tau}{\rho}$  and the logarithm of  $N$  or  $\lambda$  be used as co-ordinates, the curve will be composed of parallel rectilinear segments separated by sharp jumps; this method of plotting is often very convenient.

It can also be supposed that  $C$  is of the form

$$C = C_K + C_L + C_M + C_N \dots$$

the discontinuities of  $C$  arising from the terms of this series being at first zero, for small values of  $N$  and  $\lambda$ , and appearing suddenly one after the other. In the curve for constant  $N$ ,

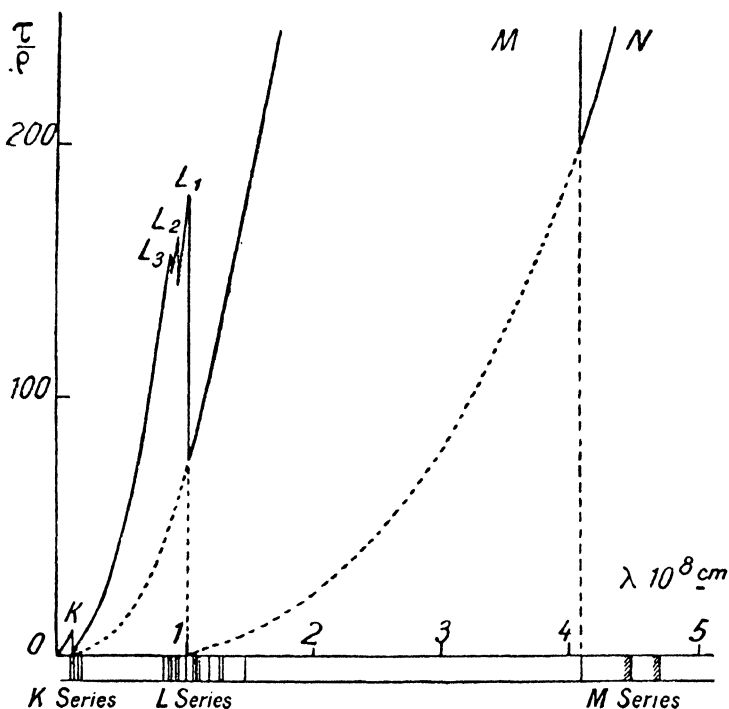


FIG. 6.

for example, the ordinate corresponding to a value of  $\lambda$  will be the sum of the ordinates of several curves

$$\frac{\tau_K}{\rho} = C_K \lambda^3$$

$$\frac{\tau_L}{\rho} = C_L \lambda^3.$$

$$\dots \dots \dots$$

**3. Variation of the absorption coefficient of an element with the wave-length.**—This is the case of Fig. 6 ( $N$  is

constant). The general trend of the curve shows that  $\frac{\tau}{\rho}$  diminishes rapidly as  $\lambda$  decreases ; this expresses the well-known fact that radiations become more penetrating as their frequency increases.

The sharp discontinuities which appear at the wavelengths  $\lambda_K, \lambda_L, \lambda_M, \dots$  indicate that at each of these wavelengths a new absorption phenomenon commences, which is directly explained by Bohr's theory.

When the frequency of the incident radiation reaches and passes the critical absorption frequency  $\nu_L = \frac{c}{\lambda_L}$ , an electron is extracted from the L level ; it will emerge as a secondary  $\beta$ -ray and the return of the atom to its normal state will be accompanied by the emission of the L series of the X-ray spectrum of the element considered.

Fig. 6 gives an idea of the variation of the absorption coefficient of a heavy element and the position of the emission lines belonging to the different series.

Each discontinuity is characterised by the value of the wave-length at which it occurs and by the magnitude of the increase in the absorption coefficient  $\tau$ , i.e. by the ratio  $\frac{\tau_1}{\tau_2}$  where  $\tau_1$  is the coefficient on one side and  $\tau_2$  on the other side of the discontinuity.

**4. Verification of Bragg and Peirce's law.**—Numerous authors have confirmed the validity of Bragg and Peirce's law, the best determinations appearing to establish definitely that the value of the index of  $\lambda$  is 3 ; some physicists have found values between 2.5 and 3, instead of 3.

The relation appears to be applicable to X-rays of all frequencies from 0.1 Ångströms to 100 Ångströms (Holweck) [2]. The general increase in the absorption by all substances at the beginning of the ultra-violet thus marks the end of the region in which the absorption coefficients are governed by this simple and general law.

TABLE VI

MASS ABSORPTION COEFFICIENTS  $\frac{\mu}{\rho}$  OF MONOCHROMATIC RADIATIONS OF SHORT  
WAVE-LENGTHS IN VARIOUS ELEMENTS. (Hull and Rice.)  
(c.g.s. units.)

$\lambda \text{ } 10^{-8} \text{ cm.}$	Al.	Cu.	Pb.
0'122 . . . .	—	—	3'00
0'147 . . . .	0'154	0'71	1'50
0'160 . . . .	0'178	0'79	1'82
0'172 . . . .	0'199	0'91	2'32
0'184 . . . . $W_{K\beta_1}$	0'218	1'07	2'71
0'196 . . . .	0'243	1'27	3'40
0'208 . . . . $W_{K\alpha}$	0'255	1'39	3'70
0'221 . . . .	0'283	1'70	4'63
0'245 . . . .	0'342	2'24	6'7
0'294 . . . .	0'493	3'84	11'1
0'343 . . . .	0'726	—	—
0'392 . . . .	0'860	—	—
Density . . . .	2'70	8'93	11'37

Richtmeyer [3] concludes from his measurements that for wave-lengths appreciably shorter than that of the  $K$  discontinuity, an element of atomic number  $N$  possesses an atomic absorption coefficient represented by

$$\frac{\tau}{\rho} A = 2.29 \cdot 10^{-2} N^4 \lambda^3,$$

where  $\lambda$  is expressed in centimetres.

According to the same author another term must be subtracted in the neighbourhood of the absorption limit.

This relation has been verified for wave-lengths as short as 0.09 Å.; but it should be noted that the coefficient of absorption of penetrating  $\gamma$ -rays seems to decrease *more rapidly* than the law indicates.

Wingardh [24] has made an extended series of measurements of the absorption coefficients of solutions, employing various solvents. He arrived at figures close to Richtmeyer's, but with the wave-length he used ( $\lambda = 0.708 \text{ Å.}$ ) the index of  $N$  appeared to be slightly less than four.

The absorption ratio  $\frac{\tau_1}{\tau_2}$  is of the order of 8 (Glocker) for the  $K$  discontinuities and tends to decrease as  $N$  increases.



TABLE VII \*

MASS ABSORPTION COEFFICIENTS  $\frac{\mu}{\rho}$  OF MONOCHROMATIC RADIATIONS OF MEDIUM WAVE-LENGTHS IN VARIOUS ELEMENTS (*c.g.s. units*)

(The values in heavy type refer to the coefficients  $\tau = \frac{\mu}{\rho} - 0.2$ .)

$\lambda \times 10^8$ cm.	Glass.	Al.	Fe.	Ni.	Cu.	Zn.	Mo.	Rh.	Pd.	Ag.	Sn.	Pt.	Au.
0.226								4.92	5.13	5.53			
0.249								6.44	8.61	9.29			
0.268								8.51	13.8	14.5			
0.273								12.9	21.5	22.8			
0.312								18.4	27.4	29.6			
0.353								32.5	45	47.8			
0.363								—	—	10.3			
0.396								58.2	11.2	12.15			
0.424								—	11.4	12.4			
0.465								—	8.4	—			
0.491—0.501	—	1.94	14.2	17.8	20.9	21.8	—	—	19.3	—	12.2	46.9	48.0
0.509—0.521	2.06	2.25	17.7	21.6	22.4	25.0	—	—	—	—	15.2	52.3	58.0
0.534—0.545	—	—	—	—	—	—	—	—	—	—	—	—	—
0.562—0.567	—	2.73	19.3	23.4	25.3	28.1	—	—	12.8	14.0	16.7	55.1	57.7
0.586—0.590	—	2.70	20.4	25.0	26.7	30.3	—	—	13.6	14.3	18.1	64.1	65.8
0.612—0.616	3.00	3.16	23.1	28.9	30.9	34.0	—	—	15.9	17.3	—	74.4	75.4
0.619—0.620	—	2.80	21.6	26.8	29.7	32.8	—	—	16.2	16.9	20.0	75.9	78.5
0.706—0.711	—	3.53	26.0	32.1	34.6	38.8	—	—	18.0	19.8	23.2	—	—
0.958	4.48	—	—	—	—	—	—	—	—	—	—	—	—
1.101—1.120	5.58	11.4	80	115	115	—	18.37	—	—	—	78	92	98
1.313	—	20.8	125	167	186	—	23.3	—	—	—	107	145	—
Density $\rho$ . . . . .	2.6	30.8	205	250	273	39.1	9.01	12.6	11.9	10.5	7.29	21.5	19.3

The atomic absorption coefficient is a function of  $N$  and may thus be used to fix the atomic mass of an element. Twenty years ago Benoist introduced the idea of the transparency equivalent of elements, which is essentially a first approximation to Bragg and Peirce's law. This property has been applied to the selection of the atomic masses of indium, thorium, and beryllium (Benoist and Copaux) [2a]. It was one of the first indications of the profound connection between high-frequency radiations and the constitution of matter.

TABLE VIIA \*

ABSORPTION COEFFICIENTS FOR THE  $\alpha$  LINE ( $\lambda = 0.586 \text{ \AA.}$ ) OF PALLADIUM

Elements.	Atomic Number.	$\frac{\tau}{\rho}$ .	$\frac{\mu}{\rho}$ .	$\frac{\mu_A}{\rho}$ .
H	1	0.0015	0.2015	$0.331 \times 10^{-24}$
C	6	0.301	0.501	9.85
N	7	0.468	0.668	15.34
O	8	0.687	0.887	23.28
F	9	0.966	1.166	36.28
Na	11	1.726	1.926	72.6
Mg	12	2.239	2.439	96.9
Al	13	2.805	3.005	133.7
Si	14	3.516	3.716	172.1
P	15	4.295	4.495	228.6
S	16	5.212	5.412	284.5
Cl	17	6.194	6.394	371.6
K	19	8.551	8.751	561.0
Ca	20	9.977	10.18	669.0
Cr	24	16.98	17.18	1463
Mn	25	19.05	19.25	1732
Fe	26	21.58	21.78	1992
Co	27	24.10	24.30	2346
Ni	28	26.79	26.99	2600
Cu	29	29.72	29.92	3112
Zn	30	32.81	33.01	3538
As	33	43.05	43.25	5315
Se	34	46.88	47.08	6115
Br	35	51.40	51.60	6755

\* E. A. Owen, *Proc. Roy. Soc.*, 1918, 94, p. 510.

# THE ABSORPTION OF X-RAYS BY MATTER 61

## TABLE VIII \*

ABSORPTION COEFFICIENTS:  $\frac{\mu}{\rho}$  IN c.g.s. UNITS

$\lambda$ .	H <sub>2</sub> O.	Al.	Cu.	Mo.	Ag.	Pb.
0.09 Å.	0.165	—	—	—	—	—
0.120	0.175	—	—	—	—	—
0.135	0.179	0.193	0.59	1.51	—	—
0.184	0.199	0.239	1.25	3.27	4.26	3.20
0.209	0.207	0.276	1.74	4.55	5.94	5.11
0.234	0.220	0.328	2.31	6.15	9.50	7.00
0.258	0.234	0.393	3.00	8.10	12.5	9.35
0.283	0.249	0.469	3.87	10.75	15.6	12.0
0.308	0.266	0.567	4.87	13.5	19.5	15.5
0.332	0.284	0.670	6.02	16.7	23.6	19.3
0.356	0.306	0.795	7.29	19.8	28.5	23.7
0.368	0.319	0.861	8.10	21.7	31.0	26.3
0.381	0.335	0.940	8.85	23.7	34.0	29.0
0.393	0.348	1.017	9.64	25.6	37.0	31.9
0.405	0.358	1.095	10.2	27.5	39.2	34.5
0.417	0.376	1.174	11.3	29.5	43.7	37.9
0.430	0.394	1.285	12.3	31.5	47.8	41.4
0.453	—	1.477	13.4	37.3	56.0	47.0
0.479	—	1.706	16.6	42.5	—	55.0
0.503	—	1.95	19.0	49.4	11.5	60.8
0.551	—	2.49	24.9	63.8	15.1	73.0
0.600	—	3.18	31.6	80.7	19.6	—
0.650	—	4.05	39.5	15.1	24.3	—
0.715	—	5.32	52.8	19.9	—	—
0.743	—	5.83	—	22.6	—	—
0.798	—	—	—	27.2	—	—
0.847	—	—	—	32.3	—	—
0.895	—	—	—	36.0	—	—
0.943	—	—	—	43.4	—	—

## TABLE IX †

ATOMIC ABSORPTION COEFFICIENTS:  $\frac{\mu}{\rho}$  Å. 10<sup>22</sup>

$\lambda$ 10 <sup>3</sup> cm.	Al.	Fe.	Ni.	Cu.	Zn.	Pd.	Ag.	Sn.	Pt.	Au.
0.491	0.86	13.0	17.2	21.8	23.4	101.5	18.2	23.8	150	155
0.508	1.00	16.2	20.8	23.4	26.8	20.0	22.0	29.7	167	188
0.537	1.22	17.7	22.6	26.4	30.1	22.4	24.8	32.6	176	187
0.554	1.20	18.7	24.1	27.8	32.4	23.8	25.3	35.4	205	213
0.576	1.41	21.4	27.9	32.2	36.4	28.3	30.0	39.0	238	244
0.615	1.57	23.8	30.9	36.1	41.6	31.5	35.1	45.5	243	254
Å. 10 <sup>22</sup>	44.5	91.6	96.4	104.3	107.1	175.0	177.0	195.2	320.3	323.5

\* Richtmeyer, *Phys. Rev.*, 1921, II, p. 13.

† Bragg and Peirce.

TABLE X

ABSORPTION COEFFICIENTS FOR WAVE-LENGTHS SLIGHTLY LESS THAN THAT OF THE K DISCONTINUITY

Aluminium . . . . .	$\frac{\mu}{\rho} = 14.45 \lambda^3 + 0.15$	The second term represents the scattering coefficient	0.1 Å. to 0.4 Å.	
	$\frac{\mu}{\rho} = 14.30 \lambda^3 + 0.16$		0.4	0.7
Copper . . . . .	$\frac{\mu}{\rho} = 147 \lambda^3 + 0.5$		0.1	0.6
Molybdenum . . . . .	$\frac{\mu}{\rho} = 450 \lambda^3 + 0.4$		0.1	0.35
Silver . . . . .	$\frac{\mu}{\rho} = 603 \lambda^3 + 0.7$		0.1	0.4

TABLE XI\*

ABSORPTION COEFFICIENTS FOR WAVE-LENGTHS SLIGHTLY GREATER THAN THAT OF THE K DISCONTINUITY.

Molybdenum . . . . .	$\frac{\mu}{\rho} = 51.5 \lambda^3 + 1$	The second term represents the scattering coefficient
Silver . . . . .	$\frac{\mu}{\rho} = 86 \lambda^3 + 0.6$	
Lead . . . . .	$\frac{\mu}{\rho} = 510 \lambda^3 + 0.75$	

### 5. The wave-lengths of the absorption discontinuities.—

The measurement of the critical frequencies, at which occur the sharp increases in the curve showing the absorption of an element as a function of the wave-length, is of considerable interest.

In fact, it is when the frequency of the radiation passes through this value that a new phenomenon is observed, characterised by the appearance of a new spectral series. Bohr's theory identifies the critical absorption frequencies with the frequencies of the energy levels, which are connected

\* Richtmeyer, *Phys. Rev.*, 1921, II, p. 13.

with the works of extraction of these levels \* by Planck's relation.

Before Laue's discovery, Barkla had been able to show that the coefficient of absorption of an element varied regularly between certain limits, but increased considerably after the region of the fluorescent rays was reached. These rays occupy a region of maximum transparency, which almost directly contradicts Kirchhoff's law.

The first spectral photographs obtained in a continuous manner (M. de Broglie [4]) at the end of 1913, showed bands with sharp edges (see Fig. 2, Plate 2), clearly indicating

(a) That the change in absorption is produced quite suddenly ;

(b) That the wave-length of the discontinuity can be determined accurately by the photography of a continuous spectrum.

The absorption bands observed on the photographs corresponded to the K discontinuities of the silver and bromine of the emulsion, the intensities being reversed because the energy which is absorbed in the photographic layer is employed in blackening the silver salt. They are to be found, of course, on all photographs.

If a screen be interposed between the tube and the plate, a sharp change in the intensity of the continuous spectrum is produced at the wave-length of the discontinuity (Fig. 3, Plate 1), as was shown for copper by M. de Broglie [5].

Several authors, particularly [27] Wagner, de Broglie, Siegbahn, Jonsson, Blake, and Duane, and Fricke, whose measurements are embodied in Table XII, have determined the positions of the absorption discontinuities either by the photographic method or by means of ionisation curves.

\* The work of extraction of a level is the work necessary to remove from the atom an electron of the level to which it refers.

TABLE XII

WAVE-LENGTHS OF THE K ABSORPTION DISCONTINUITIES OF THE ELEMENTS  
(Ångström Units.)

Elements.	Atomic Number.	Authors.				
		De Broglie and Cabrera.	Wagner.	Fricke.	Siegbahn, Jonsson.	Blake, Duane, Hu, Fricke, Shimizu, Stenström.
Magnesium . . . . .	12	—	—	9'5112	—	—
Aluminium . . . . .	13	—	—	7'9470	—	—
Silicon . . . . .	14	—	—	—	—	—
Phosphorus . . . . .	15	—	—	5'7580	—	—
Sulphur . . . . .	16	—	—	5'0123	—	—
Chlorine . . . . .	17	—	—	4'3844	—	—
Argon . . . . .	18	—	—	3'8657	—	—
Potassium . . . . .	19	—	—	3'4345	—	—
Calcium . . . . .	20	—	—	3'0633	—	—
Scandium . . . . .	21	—	—	2'7517	—	—
Titanium . . . . .	22	—	—	2'4937	—	—
Vanadium . . . . .	23	—	—	2'2653	—	—
Chromium . . . . .	24	—	—	2'0675	—	—
Manganese . . . . .	25	—	—	—	—	1'8892
Iron . . . . .	26	—	1'740	—	—	1'7396
Cobalt . . . . .	27	—	—	—	—	1'6018
Nickel . . . . .	28	—	1'485	—	—	1'4890
Copper . . . . .	29	1'388	1'375	—	—	1'3785
Zinc . . . . .	30	—	—	—	—	1'2963
Gallium . . . . .	31	—	—	—	1'1902	—
Germanium . . . . .	32	—	—	—	—	1'1146
Arsenic . . . . .	33	—	—	—	—	1'0435
Selenium . . . . .	34	1'003	—	—	—	0'9790
Bromine . . . . .	35	0'916	0'917	—	—	0'9179
Krypton . . . . .	36	0'8648	—	—	—	—
Rubidium . . . . .	37	0'812	—	—	—	0'8143
Strontium . . . . .	38	0'767	—	—	—	0'7696
Yttrium . . . . .	39	—	—	—	—	0'7255
Zirconium . . . . .	40	0'684	—	—	—	0'6872
Niobium . . . . .	41	0'648	—	—	—	0'6503
Molybdenum . . . . .	42	0'614	—	—	—	0'6184
. . . . .	43	—	—	—	—	—
Ruthenium . . . . .	44	—	—	—	—	0'5584
Rhodium . . . . .	45	—	—	—	—	0'5330
Palladium . . . . .	46	0'505	0'513	—	—	0'5075
Silver . . . . .	47	0'482	0'484	—	—	0'4850
Cadmium . . . . .	48	0'460	0'462	—	0'4629	0'4632
Indium . . . . .	49	—	—	—	—	0'4434
Tin . . . . .	50	0'421	0'422	—	0'4231	0'4242
Antimony . . . . .	51	0'401	0'405	—	—	0'4065
Tellurium . . . . .	52	0'385	0'383	—	0'3877	0'3896
Iodine . . . . .	53	0'369	0'369	—	0'3715	0'3737
Xenon . . . . .	54	0'3588	—	—	—	—
Caesium . . . . .	55	0'340	—	—	0'3436	0'3444
Barium . . . . .	56	0'327	0'331	—	0'3306	0'3307
Lanthanum . . . . .	57	0'3186	—	—	0'3186	0'3188

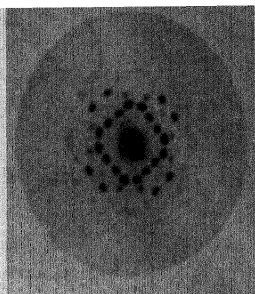


FIG. 1.—DIAGRAM OF A CUBIC CRYSTAL (zinc blende)

A

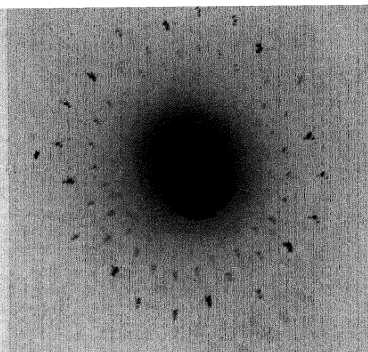
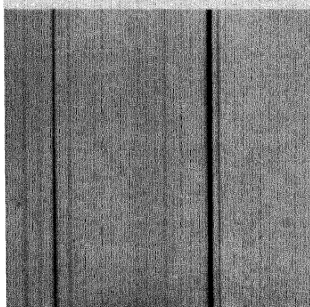
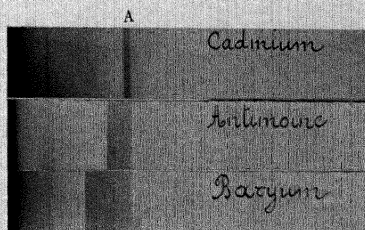


FIG. 2.—DIAGRAM OF A TETRAGONAL CRYSTAL (cassiterite)



B

FIG. 3.—AB—COPPER DISCONTINUITY (incident spectrum: tungsten)



B

FIG. 4.—ABSORPTION DISCONTINUITIES OF CADMIUM, ANTIMONY AND BARIUM

AB—Reversed Silver Band due to emulsion

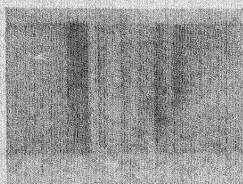


FIG. 5.—ABSORPTION SPECTRUM OF A PREPARATION OF RARE EARTHS

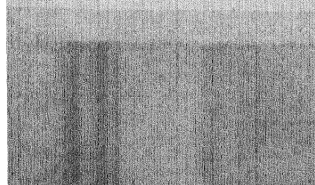


FIG. 6.—ABSORPTION SPECTRUM OF

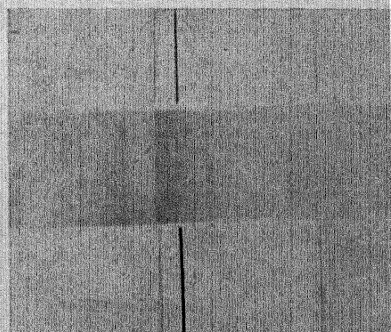


FIG. 7.—EMISSION AND ABSORPTION SPECTRA





TABLE XII—Continued

Elements.	Atomic Number.	Authors.					
		De Broglie and Cabrera.	Wagner.	Fricke.	Siegbahn, Jonsson.	Blake, Duane, Hu, Fricke, Shimizu, Stenström.	
Cerium . . . . .	58	0·3005	0·298	—	0·3064	0·3068	—
Praesodymium . . . . .	59	0·2951	—	—	0·2946	—	—
Neodymium . . . . .	60	0·2846	0·282	—	0·2835	0·2861	—
. . . . .	61	—	—	—	—	—	—
Samarium . . . . .	62	0·2644	—	—	0·2636	—	—
Europium . . . . .	63	0·2548	—	—	0·2643	—	—
Gadolinium . . . . .	64	0·2462	—	—	0·2456	—	—
Terbium . . . . .	65	0·2376	—	—	—	0·2398	—
Dysprosium . . . . .	66	0·2301	—	—	0·2294	0·2308	—
Holmium . . . . .	67	0·2218	—	—	0·2214	—	—
Erbium . . . . .	68	0·2158	—	—	—	—	—
Thulium . . . . .	69	0·2085	—	—	—	—	—
Neo-Ytterbium . . . . .	70	0·2016	—	—	—	—	—
Lutecium . . . . .	71	0·1951	—	—	—	—	—
Celtium . . . . .	72	0·1905	—	—	—	—	—
Tantalum . . . . .	73	0·1836	—	—	—	First order	Higher orders
Tungsten . . . . .	74	—	—	—	—	0·1785	0·17806
. . . . .	75	—	—	—	—	—	—
Osmium . . . . .	76	—	—	—	—	0·1683	—
Iridium . . . . .	77	—	—	—	—	—	—
Platinum . . . . .	78	0·152	—	—	0·1578	0·1582	0·1581
Gold . . . . .	79	0·149	—	—	0·1524	0·1537	0·1532
Mercury . . . . .	80	0·146	—	—	0·1479	0·1493	0·1488
Thallium . . . . .	81	0·142	—	—	0·1427	0·1448	0·1449
Lead . . . . .	82	0·138	—	—	0·1385	0·1412	0·1409
Bismuth . . . . .	83	0·133	—	—	0·1346	0·1375	0·1369
Polonium . . . . .	84	—	—	—	—	—	—
. . . . .	85	—	—	—	—	—	—
Radium Emanation . . . . .	86	—	—	—	—	—	—
. . . . .	87	—	—	—	—	—	—
Radium . . . . .	88	—	—	—	—	—	—
Actinium . . . . .	89	—	—	—	—	—	—
Thorium . . . . .	90	—	—	—	0·1127	0·1139	0·1124
Uranium X . . . . .	91	—	—	—	—	—	—
Uranium . . . . .	92	—	—	—	0·1048	0·1075	—

6. The fine structure of the discontinuities.—In general, the curve showing the sharp increases in the absorption coefficient does not only exhibit one maximum. There are actually several peaks, close together, the whole constituting a fine structure, the complexity of which increases for the discontinuities corresponding to the more exterior levels.

*Theoretical predictions of the number of absorption limits.*—In his theory of the plane atom Sommerfeld predicted one

K discontinuity, two L, three M, four N, etc., whilst experiments now show that there are one K, three L, six M, and probably nine N discontinuities in the cases of the heavy atoms (Coster, Dauvillier). Thus Sommerfeld's theory must now be considered insufficient, in spite of its success in explaining the  $L_1L_2$  doublet; this is not surprising as it is very improbable that the atom is plane. If a three-dimensional structure of the atom be postulated, the prediction of the frequencies involves calculations which are almost impossible (Landé), but Smekal [6] has shown that the number of critical discontinuities can be predicted in a simple manner. As each electron in the atom possesses three degrees of freedom its motion is characterised by three quantum numbers, the sum of which is equal to one for the K level, two for the L level, three for the M level, and so on. If it be assumed, as indicated by the principle of correspondence, that one of the quantum numbers cannot be equal to zero, it is found that the number of discontinuities when the total number of quanta is  $n$  is given by the expression  $\frac{n(n+1)}{2}$ . According to Smekal, therefore, there should be one K level, three L levels, six M levels, ten N levels, and so on. These predictions agree with the actual experimental results.

*Regular and irregular doublets.*—Each pair of levels belonging to the same layer defines what Sommerfeld calls a "doublet of fine structure." These doublets are divisible into two categories, and, in general, the doublets of one type seem to alternate with those of the other type. The difference  $\Delta\lambda$  between the wave-lengths of the two levels is constant throughout the series of the elements for doublets of the first type, called "regular doublets." The doublets of Sommerfeld's theory (notably the  $L_1L_2$  doublet) are a particular case of this type, but the theory in its present state appears to be unable to give a general explanation of all these regular doublets. The other, "irregular," doublets, have not been satisfactorily explained;\* according to

\* See, however, Sommerfeld and Wentzel, *Zeits. f. Physik*, 1921, p. 86.

Wentzel  $\Delta\sqrt{\frac{\nu}{R}}$  should be constant for these doublets, but this law appears to be only approximately true (Dauvillier [7]).

**7. K discontinuities.**—As will be seen from Table XII, the K limits have been determined for the elements from uranium to magnesium; the results obtained by various observers for the very heavy elements still show some disagreement.

It is interesting to plot the square roots of the frequencies of the discontinuities, instead of the frequencies themselves,

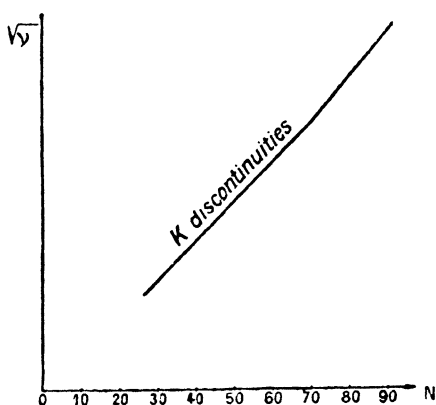


FIG. 7.

against the atomic numbers. In fact, the theory predicts that the straight line, corresponding to Moseley's law (Chapter I, p. 12), should be obtained if the frequencies of the absorption limits are used and not those of the emission lines.

The experimental results show that in the case of the K discontinuities the points lie approximately on a straight line (Fig. 7), with, however, a deviation towards higher frequencies for the elements of high atomic number. As yet, the numerical results in this region given by different authors are too far from agreement for any quantitative conclusions to be drawn concerning this deviation,

Taking the figures of Blake and Duane [25], Moseley's line for the K discontinuities satisfies the equation

$$\sqrt{\nu} = \sqrt{\nu_0}(N - 3.5).$$

Duane has suggested that the results for high frequencies would be better represented by the introduction of the electronic velocities connected with the frequencies by the quantum relation. He found that if this were done, the formula

$$\nu = \nu_0(N - 1.5)$$

was very nearly valid ;  $\nu_0$  having the value 0.00678 *c*.

Holweck, Hughes, and Richardson have obtained the values given at the end of Chapter IV for rays in the neighbourhood of the ultra-violet region, notably for the K absorption limits of carbon and aluminium.

On the other hand, the K limits of hydrogen and helium should coincide with the frequency limits of the ultra-violet series of these elements, i.e. for hydrogen, the frequency of the K discontinuity should be exactly equal to Rydberg's frequency.

If a particular level be considered, Moseley's equation can be written

$$\sqrt{\nu} = A(N - \sigma)$$

$\sigma$  being the correction which must be made to the central positive charge on account of the electrons nearer to the nucleus than the level or situated on it.

When this relation is satisfied, the curve showing  $\sqrt{\nu}$  as a function of  $N$  is a straight line. The value of  $N$  for which  $\sqrt{\nu}$  is zero, i.e.  $\sigma$ , is obtained by prolonging the line to its intersection with the  $N$  axis. Kossel [15] has called attention to the fact that the term subtracted should remain unaltered whatever the atomic number, provided that the number of electrons on the level considered remains complete (Neon ( $N = 10$ ) for the L series ; helium ( $N = 2$ ) for the K series). Moseley's curve should bend sharply at these

critical values. As a matter of fact, if the branch corresponding to Fricke's determinations for the K discontinuities of chromium and magnesium be prolonged, it is found that it cuts the axis at  $N = 2$ . The L series, which can be extrapolated by the principle of combination, affords a similar confirmation, ending at about neon ( $N = 10$ ).

The K bands are unique; their simplicity and their distribution in the continuous spectrum make them convenient for use in a method of analysis by absorption for the elements of high atomic weight. Figs. 5 and 6 of Plate I refer to specimens of the rare earths; the former contained an impure erbium nitrate and the K absorption bands of the elements, 64, 66, 68, 70 (all even) can be seen; the latter contained a didymium salt and the K bands of neodymium, praeosodymium, and lanthanum are visible.

These two photographs were obtained with exposures of only fifteen minutes.

There are as yet few papers on the sensitiveness of analysis by absorption spectra. M. de Broglie [8] found that the K band of barium could still be distinguished with an aqueous solution of 1 part in 1000.

Fig. 7 of Plate I shows the K discontinuity and the K emission lines of rhodium taken on the same plate under comparable conditions. It is seen that the wave-length of the discontinuity differs very little from that of the  $\gamma$  line (2 or 3 parts in 1000).

Fig. 4 of Plate I illustrates the progressive displacement of the K band for three elements of increasing atomic weight.

*J bands.*—Bohr's theory predicts neither a discontinuity nor a series of lines corresponding to frequencies greater than those of the K group. Barkla and Miss White [9] have interpreted small alterations in the absorption curve as indicating the presence of a J series. The existence of such a series does not appear to be established \* [10, 11].

Radiations of a frequency greater than those of the

\* In all cases, a phenomenon quite distinct from the ordinary series is concerned.

K-rays are considered to proceed from the nucleus; this will be discussed later (Chap. VI).

**8. L discontinuities.**—The bands of the L series form a multiple system, a fact which is in good agreement with theory.

Barkla had also discovered a region of selective absorption in the neighbourhood of the L series. De Broglie [12] and Wagner [13] showed that the L absorption band was resolvable into three discontinuities,  $L_1$ ,  $L_2$ ,  $L_3$ , which were most easily observed with the heavy elements. Duane

and Patterson have measured them by means of an ionisation spectrometer [14].

De Broglie has measured the two bands  $L_1$  and  $L_2$  of radium and has thus confirmed that this element has an atomic number 88. Fig. 1 of Plate 2 shows examples of the L bands (uranium and thorium).

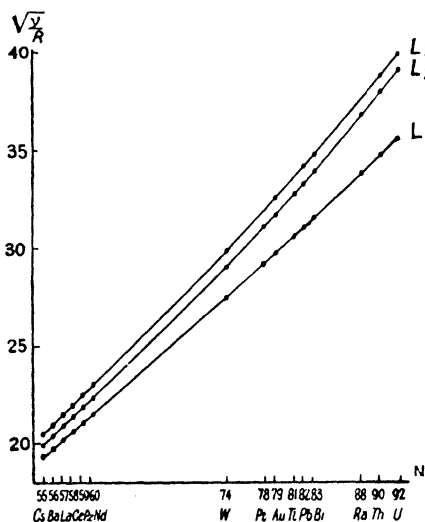


FIG. 8.

Tables XIII and XIV indicate the different values obtained for the L bands. The curves representing Moseley's law are shown in Fig. 8; it may be observed that the  $L_1$  curve is approximately a straight line, but those for  $L_2$  and  $L_3$  have an appreciable curvature.

Sommerfeld's theory predicts two levels  $L_1$  and  $L_2$  in the L layer and the difference between these levels can be calculated in terms of the "constant of fine structure." Experimental evidence supports the predictions of the theory on this latter point.

TABLE XIII  
ÅNGSTRÖM UNITS

Elements.	Atomic Number.	PHOTOGRAPHIC METHOD.						IONISATION METHOD.		
		Rock Salt: $d = 2.814 \cdot 10^{-8}$ cm.						Calcite: $d = 3.028 \cdot 10^{-8}$ cm.		
		De Broglie.			Wagner.			Duane and Patterson.		
		$L_1$ .	$L_2$ .	$L_3$ .	$L_1$ .	$L_2$ .	$L_3$ .	$L_1$ .	$L_2$ .	$L_3$ .
Tungsten	74	1.215	1.083	—	—	—	—	1.2136 $\pm$ 1	1.0726 $\pm$ 5	1.024 $\pm$ 3
Platinum	78	1.069	0.930	—	—	—	—	1.0704 $\pm$ 3	0.9321 $\pm$ 3	0.8885 $\pm$ 9
Gold	79	1.038	0.898	0.858	0.934	0.914	—	1.0383 $\pm$ 3	0.8993 $\pm$ 3	0.8606 $\pm$ 8
Mercury	80	1.006	—	—	—	—	—	1.0067 $\pm$ 5	0.8700 $\pm$ 3	0.8335 $\pm$ 9
Thallium	81	0.974	0.840	—	—	—	—	0.9776 $\pm$ 3	0.8415 $\pm$ 3	0.8055 $\pm$ 14
Lead	82	0.945	0.811	—	—	—	—	0.9497 $\pm$ 9	0.8133 $\pm$ 3	0.7803 $\pm$ 9
Bismuth	83	0.921	0.786	0.753	—	—	—	0.9216 $\pm$ 3	0.7872 $\pm$ 3	0.7532 $\pm$ 9
Radium	88	0.802	0.668	—	—	—	—	—	—	—
Thorium	90	0.757	0.624	0.604	—	—	—	0.7596 $\pm$ 3	0.6286 $\pm$ 3	0.6044 $\pm$ 7
Uranium	92	0.718	0.588	0.564	—	—	—	0.7214 $\pm$ 3	0.5918 $\pm$ 3	0.5685 $\pm$ 7

References.—De Broglie, *Jour. de Phys.*, May-June, 1916, p. 161, and Jan., 1919, p. 31. Wagner, *Ann. der Phys.*, March, 1915. Duane and Patterson, *Nat. Acad. Proc.*, Sept., 1920.

TABLE XIV\*

WAVE-LENGTHS OF THE L ABSORPTION DISCONTINUITIES OF THE ELEMENTS  
Cs — Nd.

Elements.	Atomic Number.	$\lambda$ in Å.		
		L <sub>1</sub> .	L <sub>2</sub> .	L <sub>3</sub> .
Caesium . . . .	55	2'459	2'299	2'157
Barium . . . .	56	2'348	2'194	2'063
Lanthanum . . . .	57	2'250	2'098	1'971
Cerium . . . .	58	2'158	2'007	1'887
Praesodymium . . . .	59	2'071	1'922	1'808
Neodymium . . . .	60	1'992	1'842	1'736

TABLE XIVA

THE L ABSORPTION DISCONTINUITIES OF THE ELEMENTS FROM  
ANTIMONY TO IRIDIUM

Elements.	Atomic Number.	$\lambda$ in Å.		
		L <sub>1</sub> .	L <sub>2</sub> .	L <sub>3</sub> .
Sb † . . . .	51	2'9945	2'8310	2'6327
Te . . . .	52	2'8410	2'6387	2'5026
I . . . .	53	2'7124	2'5483	2'3819
Xe ‡ . . . .	54	2'5875	2'4253	2'2724
Cs † . . . .	55	2'4678	2'3073	2'1605
Ba . . . .	56	2'3577	2'1995	2'0602
Ce § . . . .	58	2'1597	2'005	—
Pr . . . .	59	2'0727	1'9197	—
Nd . . . .	60	1'9903	1'8376	—
Sa . . . .	62	1'8409	1'701	1'608
Eu . . . .	63	1'773	—	—
Gd    . . . .	64	1'699	1'550	1'470
Dy . . . .	66	1'576	1'435	1'362
Er . . . .	68	1'478	1'336	1'265
Yb . . . .	70	1'386	1'242	1'171
Ct § . . . .	72	1'2930	1'1515	1'097
Ta    . . . .	73	1'253	1'111	1'058
W . . . .	74	1'211	1'071	1'023
Os . . . .	76	1'138	0'998	0'951
Ir . . . .	77	1'103	0'965	0'919

\* G. Hertz, *Zeits. f. Phys.*, III, pp. 19-25, 1920 (Ångström units).

† Lindsay, *Comptes Rendus*, 1922, II, p. 151.

‡ Lepape and Dauvillier, *Comptes Rendus*, 1923, I-II, p. 34.

§ Coster, *Phil. Mag.*, 1922, II, p. 546.

|| Cork, *Phys. Rev.*, March, 1923, p. 326.



**9. M discontinuities.**—So far there are not many direct numerical results concerning the M levels. Stenström has given the results for uranium, thorium, and bismuth which are embodied in Tables XV and XVI.

TABLE XV \*

WAVE-LENGTHS OF THE M DISCONTINUITIES OF THE ELEMENTS  
(Ångström Units.)

Elements.	Atomic Number.	PHOTOGRAPHIC METHOD. Rock Salt: $d = 2.814 \cdot 10^{-8}$ cm.			
		M <sub>1</sub> .	M <sub>1</sub> .	M <sub>2</sub> .	M <sub>3</sub> .
Thorium . .	90	3.721	—	3.552	3.058
Uranium . .	92	3.491	3.459	3.326	2.873

TABLE XVI †

Elements.	M <sub>1</sub> .	M <sub>2</sub> .	M <sub>3</sub> .	M <sub>4</sub> .	M <sub>5</sub> .
Bismuth . .	4.762	4.569	3.894	—	—
Thorium . .	3.721	3.552	3.058	2.571	2.388
Uranium . .	3.491	3.326	2.873	2.385	2.228

**10. Discontinuities of higher orders, N, O, P, . . .**—No direct information is available, as yet, concerning the frequencies of the N, O, P, . . . absorption discontinuities, though there is no doubt that they exist. Nevertheless, as the principle of combination of emission lines is firmly established in the region where the discontinuities are known, the existence of these levels can be inferred and their critical absorption frequencies calculated from emission spectra. This question will be considered in greater detail in the next chapter which deals with emission spectra.

\* Wilhelm Stenström, Lund, 1919.

† D. Coster, *Phys. Rev.*, 1922, 19, p. 20 (Ångström Units).

**11. The existence of fringes in the immediate neighbourhood of the absorption discontinuities.**—Kossel has drawn attention to the fact that the explanation usually given of the absence of absorption lines (Fraunhofer lines) in X-ray absorption spectra (namely, that an electron cannot jump from one level to a level further away from the nucleus because, in general, there is not a place at its disposal) should not apply to the peripheral levels. The existence of the phenomenon of the reversal of lines in luminous spectra proves, in fact, that this transfer of an electron towards the exterior is possible in the peripheral zone. For example, if a corpuscle jumps from the K level to a peripheral level, linear absorption will occur at a frequency only very slightly less than that of the K discontinuity. It should be possible therefore, to observe a group of absorption lines in the neighbourhood of the discontinuity, giving a “fine structure” to the head of the discontinuity. That would be the *residuum* of optical phenomena, where the influence of chemical combination and external forces should be felt.

Stenström [17] was the first to discover the existence of fringes in the neighbourhood of an absorption discontinuity, on the low frequency side.

Hertz [18] has also described appearances of this nature in the L bands of the rare earth elements (caesium, neodymium) and states that the region in which they appeared justifies Kossel's ideas.

H. Fricke [19] when investigating the K discontinuities of the elements from magnesium to chromium, found a complex fine structure extending over a range of wavelengths of about 0.02 to 0.04 Å. (corresponding to approximately 30 to 70 volts) at the edges of the absorption bands of phosphorus, sulphur, chlorine (NaCl), potassium ( $K_2CO_3$ ), calcium ( $CaCO_3$ ), titanium ( $TiO_2$ ), vanadium ( $V_2O_5$ ), and chromium ( $K_2CrO_4$ ). He also studied the variations of intensity in this region photometrically. The outstanding feature of his photographs is the existence of a white line separating the impressions corresponding to the two sides of

the discontinuity ; with sulphur, in particular, another white line separated from the first by a small dark space can clearly be distinguished.

M. de Broglie and A. Dauvillier [26], and Coster have mentioned several cases in which continuous X-ray spectra have shown white lines. The phenomenon has been especially clearly observed in the emission from a barium anticathode ; a very fine white line is found exactly at the position of the  $L_1$  and  $L_2$  discontinuities. It is not a question of the reversal of an emission line but of the presence of an absorption line in the same position as an absorption discontinuity ; a fact which has not yet been satisfactorily explained.

**12. The influence of the chemical state on the frequencies of the absorption discontinuities of light elements.**—The absorption of X-rays is an atomic phenomenon and Holweck's results, for example, indicate that this character persists up to rays of long wave-length ( $\lambda = 100 \text{ \AA.}$ ). It may be questioned, however, whether the position of the absorption bands, which depends on the complete electronic configuration, is altogether independent of the chemical state, in the case of the light elements. So far, two investigators have announced influences of this nature.

Berengren [20] measured the K absorption discontinuities of various screens containing phosphorus in different states. Ammonium phosphate and phosphoric acid showed a discontinuity at  $\lambda = 5.750 \text{ \AA.}$  whilst in the case of Bridgeman's black phosphorus it was at  $\lambda = 5.767 \text{ \AA.}$  (the dispersion was such that in the region considered 1 mm. on the photographic plate corresponded to  $0.055 \text{ \AA.}$ ) ; red phosphorus showed both these lines simultaneously. This result seems to show that in this region the position of the K bands is affected at least by the allotropic condition.

Lindh [21] examined the K discontinuity of chlorine, using the gas itself, monovalent compounds of chlorine ( $\text{LiCl}$ ,  $\text{NaCl}$ , etc.), and other compounds in which it had valencies of five and seven ( $\text{KClO}_3$ ,  $\text{KClO}_4$ ). From his results he concluded that the discontinuity is the same for

chlorine and its monovalent compounds ( $\lambda = 4.384 \text{ \AA.}$ ). The wave-length of the discontinuity in the case of  $\text{KClO}_3$  was  $0.06 \text{ \AA.}$  less, and in the case of  $\text{KClO}_4$ ,  $0.012 \text{ \AA.}$  less than this value. The fine structure described by Fricke could be distinguished at the edge of the bands (this obviously made the measurements more difficult).

Quite recently [23] new researches by Lindh have shown that the same effect obtains for sulphur, being even more marked in this case. When the absorption limit of crystalline sulphur was compared with that of the same element in gypsum, it was found that the K discontinuity of the sulphur in the latter crystal had an appreciably shorter wave-length. The author then examined several sulphur compounds of different types; compounds in which the valency of the sulphur was two ( $\text{Na}_2\text{S}$ ,  $\text{CaS}$ ,  $\text{CuS}$ ), four ( $\text{Na}_2\text{SO}_3$ ,  $\text{CuSO}_3$ ), and six ( $\text{Li}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{CuSO}_4$ ). As in the case of chlorine, the K absorption limits are displaced towards the region of short wave-lengths as the valency increases, compounds in which the sulphur has the same valency showing the same discontinuities.\* When the valency changed from two to four and from two to six the wave-length decreased by  $0.014$  and  $0.022 \text{ \AA.}$  units ( $7$  and  $11$  volts) respectively. The compounds in which the valency was four also showed the discontinuity corresponding to the valency of six. The wave-length of the K discontinuity of sulphur is at about five  $\text{\AA.}$ , i.e. about  $2470$  volts; it is conceivable, therefore, that chemical combination might have an effect on levels which are sufficiently superficial.

**13. Theoretical predictions concerning absorption phenomena.**—As the mechanism of the phenomena of absorption is unknown at the present time the theoretical investigation of this problem is scarcely possible except by thermodynamic methods. In this connection the examination of

\* The author believes that a very small displacement of the discontinuities occurs when the associated element is changed even though the valency remains unaltered.

the equilibrium between the atom and radiation in an enclosure at a given temperature is very instructive and leads to Bragg and Peirce's law, if certain assumptions are made (L. de Broglie [22]).

One of the first consequences of the necessary existence of a thermal equilibrium is the rigorous validity of Kirchhoff's law. When in this state of equilibrium, matter must emit as much of each frequency as it absorbs. For every mechanism emitting a given frequency there must be a corresponding mechanism absorbing the same frequency. It follows that there must be an inverse photoelectric effect corresponding to the photoelectric effect, since an electron placed on the energy level  $h\nu_c$  can be expelled from the atom by a radiation of frequency  $\nu$  with an energy  $h\nu - h\nu_c$ , and an electron arriving at the atom with this energy  $h\nu - h\nu_c$ , finding a vacant place on the level  $h\nu_c$ , will be able to occupy it, giving rise to the emission of a quantum  $h\nu$  of the radiation  $\nu$ . In other words, the existence of an absorption band involves that of an emission band in the same spectral region. This is the classical result in the case of spectral lines; an absorption line corresponds to each emission line.

At first sight it would appear that the rigorous conclusions of the theory disagree with the results of experiment in the X-ray region. Absorption bands and emission lines have been known for several years but no emission band has been definitely observed, and the spectral lines have never been found to exhibit the phenomenon of reversal. This contradiction can be easily explained. Under the usual conditions of experiment the X-rays employed are much more intense than they would be in the spectrum of black body radiation at the temperature of the laboratory. Hence the phenomena which lower the frequency and thus tend to the re-establishment of thermal equilibrium will be much the more intense. This explains the practical absence of mechanisms which increase the frequency (emission bands and absorption lines) and the constant degradation of high-frequency quanta.

If the question of the reversal of lines be examined

more fundamentally, it is seen that this phenomenon must be localised in the immediate neighbourhood of the heads of the series, but that its range should be extended at higher temperatures. Reversal of the ordinary optical lines will be found to occur at these temperatures because this effect depends, as do many others, on the quotient  $\frac{h\nu}{\kappa T}$ .

*Theoretical calculation of the coefficient in Bragg and Peirce's law.*—A collection of atoms and electrons in equilibrium with black body radiation at a temperature  $T$  obeys the canonical distribution law. That is to say, if atoms are present in different states,  $J_1, J_2, J_3, \dots, J_n$ , characterised by the energies  $W_1, W_2, W_3, \dots, W_n$ , the number of atoms in the state  $J_n$  will be proportional to  $e^{-\frac{W_n}{\kappa T}}$ , and the exchanges of energy between the constituents of this system must not affect this distribution. If this principle be applied to the phenomena of absorption and emission as they are revealed by experiment the following conclusions can be drawn: "In the interior of each band the absorption is due to the superposition of the separate effects of all the bands for which the frequency of the head is less than the frequency considered, and each of these effects varies as the cube of the wave-length." This can be extended by making some rather arbitrary assumptions, which seem to be verified by their consequences, and by calling on the principle of correspondence. The complete expression for the atomic absorption coefficient for a wave-length  $\lambda$  then becomes

$$\frac{\tau A}{\rho} = \frac{\pi e^2}{c^2 m} \lambda^3 \sum_p n_p \nu_p^3$$

where  $c$  is the velocity of light,  $e$  and  $m$  the constants of the electron, and  $n_p$  the number of electrons which normally occupy the level  $h\nu_p$ . The sum  $\Sigma$  is taken over all the levels whose effects are superposed as has been stated above.

Thus by making use of the relation  $\nu_k = R N^2$  ( $R$  = Rydberg's constant =  $3.27 \cdot 10^{15}$  sec.<sup>-1</sup>) given by Bohr's

theory and verified experimentally, the absorption coefficient in the K band assumes the value

$$\left(\frac{\tau A}{\rho}\right)_K = \frac{\pi e^2}{c^4 m} R^2 \left[ n_K + n_{L_1} \left(\frac{\nu_{L_1}}{\nu_K}\right)^2 + n_{L_2} \left(\frac{\nu_{L_2}}{\nu_K}\right)^2 + \dots \right] \lambda^3 N^4.$$

By identifying this equation with Bragg and Peirce's law,  $\left(\frac{\tau A}{\rho}\right)_K = A_K \lambda^3 N^4$ , it is found that  $A_K = 2.3 \cdot 10^{-2} \text{ cm.}^{-1}$ , which is in very good agreement with the most recent experimental determinations. In addition, the coefficient  $A_K$  varies very slightly with the atomic number since it involves the ratios  $\frac{\nu_K}{\nu_{L_1}}$ , etc. For the very light elements the variation may be considerable on account of the progressive disappearance of the levels normally occupied.

At each critical frequency the coefficient  $\frac{\tau A}{\rho}$  experiences an increase which is defined as the ratio of its values for two frequencies which are very close together but which lie on either side of the critical frequency. These increases thus determine for any substance the mutual ratios of the various constants for the different branches of the  $\lambda^3$  curve which expresses Bragg and Peirce's law. The K increase is very well known: it is equal to 13 for aluminium, decreases slowly as the atomic weight increases; is equal to 7 for silver, and tends towards 5 for the heavy elements. These values and their variations satisfy the formula given above. The L increases are not so well known, but also agree with the theory which indicates exactly their relative values. A more exact determination of these increases would permit the confirmation of the distribution of the electrons among the groups of levels such as is indicated by the periodicity of the elements, and even enable us to find the distribution of the electrons of a group between the different levels of that group.

By adopting a point of view approaching that of the classical electromagnetic conceptions, A. H. Compton has obtained a formula for  $\left(\frac{\tau A}{\rho}\right)_K$  which only differs from the fore-

going by the presence of a factor equal to 2. More recently Kramers [28] has given a theory of absorption based on the principle of correspondence ; he arrives at a formula giving  $\left(\frac{\tau A}{\rho}\right)_K$  which is identical with that given above multiplied by

$$\frac{16}{3\sqrt{3}\pi} = 0.98$$

approximately. Thus all these attempts have led to analogous results ; that of Kramers appears to be most satisfactory in principle, but even it involves some arbitrary hypotheses.

**14. The special behaviour of the atomic absorption coefficient with long wave-lengths.**—In spite of the existence of discontinuities, the path of the absorption curve indicates an increase in absorption as the wave-length increases. This means that in the formula given above the disappearance of one of the terms of the sum  $\Sigma$  is rapidly compensated by the increase in the factor  $\lambda^3$ . How is it, then, that visible light can traverse some material media, such as gases, without appreciable diminution in intensity ? Bohr's theory easily explains this. In every atom in the normal state there is one level the energy of which is less than that of the other levels. The frequency assigned to this " optical level " by the quantum relation, is situated in the extreme ultra-violet for all substances ; it corresponds, moreover, to the potential at which ionisation first occurs. A radiation, the quantum of which is slightly greater than the energy of the optical level, will be able to remove an electron therefrom and the high value of the absorption in this region of the spectrum is explained by the great ease with which this removal can be performed. But if the incident radiation has a frequency less than that of the optical level, an electron cannot be removed ; there is absolute transparency. This is expressed analytically by the disappearance of the last term of the sum given above. After having attained a very large maximum value the absorption falls sharply to zero for a wave-length situated



in the ultra-violet. This wave-length varies from one substance to another and is connected with the ionisation potential of the absorbing substance by the quantum relation. Holweck's experiments, on the whole, seem to agree with these results.

It is well known that absorption phenomena are again encountered in the domain of ordinary optics, but these are due to very different causes, such as the motion of the electrical centres in conductors, or some kinds of "resonance," also governed by quanta, of the molecular structure. We are not here concerned with these causes.

# BIBLIOGRAPHY

1. W. H. BRAGG and S. E. PEIRCE, *Phil. Mag.*, 1914, 2, p. 626.
2. HOLWECK, *Thèse de doctorat*.
3. RICHTMEYER, *Phys. Rev.*, 1921, 1, p. 228, and 1921, 2, p. 13.
4. M. DE BROGLIE, *Comptes Rendus*, Nov. and Dec., 1913 and first half of 1914.
5. M. DE BROGLIE, *Comptes Rendus*, 1914, 158, p. 1493.
6. SMEKAL, *Zeits. f. Phys.*, 1920, 1, p. 309; 1920, 3, p. 243; 1920, 4, p. 26.
7. A. DAUVILLIER, *Comptes Rendus*, 1921, various papers.
8. M. DE BROGLIE, *Jour. de Phys.*, 1919, p. 1.
9. BARKLA and MISS WHITE, *Phil. Mag.*, 1917, 2, p. 270.
10. DUANE and SHIMIZU, *Phys. Rev.*, 1919, 2, p. 389.
11. A. DAUVILLIER, *Comptes Rendus*, 1919, 1, p. 608; book on *La Physique des rayons X*, p. 85.
12. M. DE BROGLIE, *Comptes Rendus*, 1916; *Jour. de Phys.*, 1916, p. 61, and 1919, p. 31.
13. WAGNER, *Ann. der Phys.*, 1915.
14. DUANE and PATTERSON, *Acad. of Sciences, Washington*, Sept., 1920.
15. KOSSEL, *Zeits. f. Phys.*, 1920, 2, p. 470.
17. STENSTRÖM, *Thesis, Lund*, 1919.
18. HERTZ, *Phys. Zeits.*, 1920, p. 630.
19. H. FRICKE, *Phys. Rev.*, 1920, 2, p. 202.
20. BERENGREN, *Comptes Rendus*, 1920, 2, p. 624; *Zeits. f. Phys.*, 1920, 3, p. 247.
21. LINDH, *Comptes Rendus*, 1921, 1, p. 1175.

22. L. DE BROGLIE, *Rayons X et équilibre thermodynamique. Jour. de Phys.*, 1922, p. 33.
23. LINDH, *Comptes Rendus*, July, 1922.
24. WINGARDH, *Zeits. f. Phys.*, 1922, p. 363.
25. BLAKE and DUANE, *Phys. Rev.*, 1917, 2, p. 697.
26. M. DE BROGLIE and A. DAUVILLIER, *Comptes Rendus*, 1920, 171, p. 626 and 1922, 174, p. 1546; and A. DAUVILLIER, *Comptes Rendus*, 1921, 173, p. 35.
27. DE BROGLIE, *Jour. de Phys.*, May-June, 1916, p. 161, and *Comptes Rendus*, March, 1920, p. 725.  
WAGNER, *Ann. der Phys.*, March, 1915.  
BLAKE and DUANE, *Phys. Rev.*, July, 1917, p. 98, and Dec., 1917, p. 698.  
DUANE and HU, *Phys. Rev.*, June, 1918, p. 488, and Dec., 1919, p. 516.  
DUANE and SHIMIZU, *Phys. Rev.*, Feb., 1919, p. 159, and Dec., 1919, p. 523.  
SIEGBAHN and JÖNSSON, *Phys. Zeits.*, 1919, p. 251.  
FRICKE, *Phys. Rev.*, Sept., 1920, p. 202.  
DUANE, FRICKE, and STENSTRÖM, *Nat. Acad. Proc.*, Sept., 1920,
28. A. H. KRAMERS, *Phil. Mag.*, 46, 1923, p. 836.
29. TAYLOR, *Phys. Rev.*, Dec., 1922, p. 709.
30. RICHTMEYER, *Phys. Rev.*, April, 1923, p. 478.

## CHAPTER IV

### PART I

#### THE CONTINUOUS SPECTRUM

**1. The emission of X-rays.**—X-rays are emitted when matter has incident on it :—

(1) Electrons of sufficiently large velocity ; this is the case of the ordinary X-ray tube, in which cathode rays bombard the anticathode giving rise to X-rays, whether the tubes be of the old gas type or whether they are of the Coolidge type with an incandescent cathode.

(2) A beam of primary X-rays which produces secondary or fluorescent radiation.

The  $\alpha$ -rays also appear to excite a secondary X- or  $\gamma$ -ray emission.

Let us consider the first case, which corresponds to the production of X-rays in tubes. It is known that the anticathode of such a tube when working emits a spectrum which consists of a continuous spectral background with bright lines, characteristic of the element of the anticathode, superposed thereon. The mechanism of the emission of the continuous spectrum seems to be distinct from that of the lines and will be considered first.

The continuous background, which is also called " general radiation " or " independent radiation " (because its nature does not depend on the anticathode used) \* is composed of an infinite number of frequencies, as is the spectrum of white light. It was formerly attributed entirely to the radiation

\* The total intensity and the distribution of the energy due to each spectral element throughout the spectrum, depend on the anticathode.

which arises according to the electromagnetic theory when electrons are accelerated [1]. In penetrating the anticathode the electrons are decelerated by the atomic fields, the magnitude and the direction of their velocities undergo changes, and an emission of radiation, such as it is desired to explain, results.

If the acceleration of the electrons be conceived as producing, not trains of waves but isolated pulses, the periodic phenomena can be explained by means of Fourier's analysis. It has been shown, however, by Webster [2], in particular, that this treatment yields a spectrum which is not limited on the high frequency side, and this is contrary to experience.

The most characteristic feature of the continuous spectrum has been brought out by the following experiments.

**2. The limit of the continuous spectrum emitted by an anticathode bombarded by cathode rays of given energy.**—When a hot cathode tube is run at a constant potential  $V$  the energy of the electrons when they strike the anticathode is  $eV$  which can be varied at will by altering  $V$ .

The radiation is analysed by means of a spectrometer provided with an ionisation chamber, by means of which the rays reflected from the crystal at various angles are examined, using the observed ionisation as a measure of the intensity of the rays.

In this way two kinds of curves can be drawn: (a) curves which are really spectra and which are obtained by measuring the intensities of ionisation for various wave-lengths when the potential applied to the tube is constant. Naturally we are only concerned here with the successive wave-lengths of the continuous spectrum and not with lines: curves of this type are shown in Fig. 9; (b) if the angle of reflection be kept constant, i.e. if a particular wave-length is examined, curves can be drawn showing how the intensity of this wave-length varies with the applied potential  $V$ . Wagner has called such curves isochromatic curves.

Whichever way the radiation is investigated the same result is obtained, namely, that the intensity of the con-

tinuous spectrum becomes zero for a radiation of a certain maximum frequency  $\nu_0$ , accurately related to the applied potential by the quantum relation

$$\nu_0 = \frac{eV}{h}.$$

Thus, in Fig. 9, which shows a series of curves each of them obtained at constant potential  $V$ , the limit  $\lambda_0$  of the continuous spectrum in every case corresponds to a frequency  $\nu_0$  equal to  $\frac{eV}{h}$ .

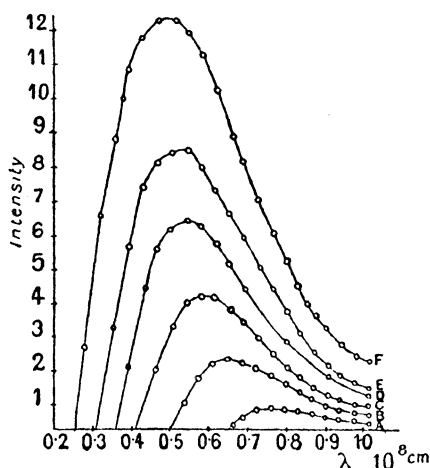


FIG. 9.

If isochromatic curves be drawn (Fig. 10), each of them cuts the horizontal axis at a value of the potential,  $V$ , connected with the wave-length  $\lambda_0$  for which it was drawn by the same relation.

To obtain from these curves the points which correspond to the limits, the curves must be extrapolated to their points of intersection with the horizontal axis. The shape of the curve enables this to be done very exactly and it is, perhaps, the best method of determining accurately the value of the constant  $h$ .

*Measurement of  $h$ .*—This law has been verified by

numerous investigators. Duane and Hunt [4] have described experiments for evaluating the minimum wavelength emitted by a Coolidge tube at constant potentials of between 25,000 and 39,000 volts (batteries of accumulators) and they have obtained a value of  $h = 6.37 \cdot 10^{-27}$  erg-seconds. Rutherford [5] attacked the same problem using very high potentials (up to 175,000 volts obtained from a statical machine), but he estimated the wave-lengths, and therefore the frequencies, by the extrapolation of a law of absorption for lead. This must vitiate the results because

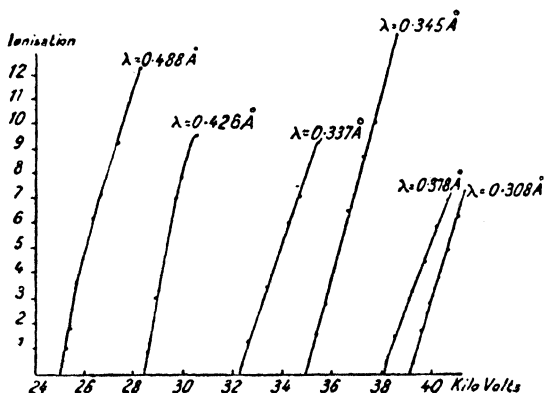


FIG. 10.

lead has an absorption band beginning at  $\lambda = 0.138 \cdot 10^{-8}$  cm., in the region examined.

Hull [6] repeated Rutherford's experiments and showed that Planck's law applies accurately between 24,000 and 100,000 volts, and that the absorption band accounts for Rutherford's results.

Ledoux-Lebard and Dauvillier [7] photographically examined the end of the continuous spectrum from a tungsten anticathode using a rotating crystal.

Blake and Duane [8] have carried out accurate measurements of the value of  $h$ , making various corrections necessitated by the size of slits, the penetration of the rays into

the crystal, etc. Their determinations were made at potentials of between 36,000 and 42,000 volts, and their final value for  $h$  was  $6.555 \cdot 10^{-27}$  erg-seconds. They think that the X-ray method is the most accurate of all those by which Planck's constant can be determined.

In a first series of measurements Wagner [9] worked with low tensions, between 4600 and 10,000 volts, and found  $h = 6.49 \cdot 10^{-27}$  erg-seconds, but in a new and more accurate determination [59] the same author has found as the mean of several experiments at different potentials

$$h = (6.53 \pm 0.01) \cdot 10^{-27} \text{ erg-seconds.}$$

Finally, Birge [10] has discussed in detail the accuracy of the various methods of finding  $h$ . He estimates that this quantity is known with an error of not more than 0.4 per cent., giving as the most probable value

$$h = 6.5543 \cdot 10^{-27} \text{ erg-seconds.}$$

This value is obtained by assuming that  $e = 4.774 \cdot 10^{-10}$  electrostatic units. This atomic charge  $e$  is the most uncertain value involved in the calculation of  $h$  by the relation  $eV = h\nu$ ,  $V$  and  $\nu$  being measured directly.

The values of  $h$  obtained by different observers using the limit of the continuous X-ray spectrum are summarised in the following table :—

DUANE and HUNT	( <i>Phys. Rev.</i> , Aug. 1915, p. 166)	. . .	$6.51 \cdot 10^{-27}$	erg-sec.
HULL	( <i>Phys. Rev.</i> , Jan. 1916, p. 156)	. . .	$6.59 \cdot 10^{-27}$	„
D. L. WEBSTER	( <i>Phys. Rev.</i> , June, 1916, p. 559)	. . .	$6.53 \cdot 10^{-27}$	„
BLAKE and DUANE	( <i>Phys. Rev.</i> , Dec. 1917, p. 624)	. . .	$6.555 \cdot 10^{-27}$	„
MULLER	( <i>Phys. Zeits.</i> , Nov. 1918, p. 489)	. . .	$6.58 \cdot 10^{-27}$	„
WAGNER	( <i>Ann. der Phys.</i> , Dec. 1918, p. 401)	. . .	$6.63 \cdot 10^{-27}$	„

It should be mentioned that Ladenburg [60], reviewing all the methods by which  $h$  has been determined, concludes that the value is  $6.54 \cdot 10^{-27}$  to within 0.2 per cent.

**3. The distribution of the energy between the wavelengths in the continuous spectrum.**—The very accurate and important result which has just been discussed puts beyond doubt the part played by quanta in the emission

of the continuous spectrum. It allows it to be said that even if part of this spectrum must be explained in a manner in accordance with the electromagnetic theory, it can only be a part of the phenomenon. To explain the continuous spectrum it will be necessary to have recourse to quantum considerations.

Unfortunately our knowledge of the conditions under which electrons are decelerated and stopped in matter is still insufficient for a satisfactory theoretical explanation to be attempted.

The variation of the intensity with the wave-length in the continuous spectrum emitted by an anticathode, using a constant difference of potential  $V$ , is shown in Fig. 9. It is seen that the intensities present the following characteristics; after a sharp beginning on the side of short wave-lengths they rise to a maximum, and then decrease less rapidly as the wave-length increases.

If a series of such curves, drawn for increasing potentials, be considered, it is observed that the commencement of the curves moves towards high frequencies in accordance with the quantum relation; the frequency of the maximum ordinate moves in the same direction and the total energy, i.e. the area of the curve, increases approximately proportionally to  $V^2$ . At the same time the value of the maximum ordinate increases rapidly and the shape of the curve becomes more pointed for high potentials.

These features suggest a comparison with the curve giving the variation with the wave-length of the intensity in the spectrum of a black body at a given temperature  $T$ . The curves are roughly analogous if the potential difference is replaced by a function of the absolute temperature. There is, however, an essential difference. The beginning of the curve on the short wave-length side is quite abrupt in the case of X-rays, wave-lengths less than a certain value being entirely absent, whilst this is not so with the curve for the emission of a black body. There is, further, no similarity between the conditions of the emission by anticathodes and



the perfectly diffused equilibrium radiation which obtains in the theory of a black body.

Bergen Davis [11], L. Brillouin [12], and Webster [13] have suggested formulæ to represent the distribution of intensity in the continuous spectrum. They can only be considered as tentative, and, moreover, it is difficult to compare their predictions with the results of experiment.

Curves such as those shown in Fig. 9 should not be regarded as giving the actual intensities of the various radiations which are emitted by the anticathode. Numerous corrections, difficult to estimate, would be necessary to convert the measured ionisation intensities into the actual intensities of emission. Dauvillier [14] has made these corrections, so far as it is possible to do so, and has been able to show how greatly the shape of the curves is modified thereby; he has also called attention [73] to the law of the displacement of the maximum ordinate of the curve. To a first approximation the experimental law which relates the wave-length of the maximum to the limiting wave-length is

$$\lambda_{max} = 1.3\lambda_0.$$

This relation has been found to hold between 20,000 and 80,000 volts.

A. H. Kramers, in a paper previously mentioned [62], has given a formula representing the intensity distribution in the continuous spectrum, using only the principle of correspondence. This formula,  $I_\nu d\nu = CN(\nu_0 - \nu)d\nu$ , where  $N$  is the atomic number and  $\nu_0$  the limiting frequency, appears to be in good agreement with the results recently published by H. Kuhlenskampff [63], according to which the intensity  $I_\nu$  is an almost linear function of  $\nu_0 - \nu$ . Kramers' theory seems to be the best which we possess at present.

**4. The variation of the intensity of the continuous spectrum with the element used as anticathode, and the efficiency of an X-ray tube.**—The radiation from an anticathode is of the type shown in Fig. 2, Chapter V, i.e. it consists of a continuous spectrum with lines superposed

thereon. When the conditions are such that the lines are not excited \* (if low potentials are used), only the continuous spectrum is obtained. If the potential is increased the alteration of the emission with the applied voltage can be followed, and when the critical excitation voltage of a series of lines is passed the law observed is found to change on account of the increased emission due to the new radiations. If the anticathode has not a high atomic weight, these radiations are easily absorbable and thus the phenomena due to the penetrating part of the general radiation can be observed by interposing a screen.

The intensity of the general radiation emitted will be measurable by the area of the curve representing the intensity of the continuous spectrum as a function of the wave-length. This general radiation can be studied either with respect to the element used as anticathode, or, for a given element, with respect to the energy possessed by the cathode rays when they strike the anticathode, i.e. with respect to the voltage applied to the tube.

Except in the case of an exceedingly thin anticathode the absorption in the anticathode itself has an effect which it is difficult to estimate.

*The variation of the emission with the nature of the anticathode.*—A long time ago Kaye [15] measured the intensity of the general radiation for about twenty elements, working with potentials of the order of 25,000 volts. He found that the intensity of the continuous spectrum was proportional to the atomic weight of the anticathode to a first approximation. Brainin [16] has confirmed Kaye's law, but has noted certain characteristics, the significance of which is not yet quite clear. Duane and Shimizu [17] have extended these measurements and have shown that the area of the curves is a function of the atomic number, rather than of the atomic weight of the anticathode. Ulrey [18] has compared the emissions of chromium, nickel, molyb-

\* See later, Chapter IV, p. 98.

denum, palladium, and tungsten, working, with great care, at potentials in the neighbourhood of 35,000 volts. He has observed that the curves for different elements are not absolutely similar, and that the total intensities, whilst obeying the atomic number law approximately, appear to exhibit also a periodicity akin to that of Mendéléeff's table.

*The variation of the emission with the applied voltage.*—A very large number of observers [19], Dorn, Wien, Carter, Angerer, Rutherford and MacClung, Beatty, Rutherford and Barnes, have investigated this variation and agree in stating that the emission of the continuous spectrum increases as the square of the potential (if the energy supplied is constant). Weeks [20], however, has found a more rapid variation with the applied voltage, but his results may have been affected by extraneous effects.

The reader will find much information on these questions in the recent papers by Wagner and Kuhlenkampff [64], Kirkpatrick [65], and Webster [66].

*The efficiency of an X-ray tube.*—The results mentioned in the preceding paragraphs show that the efficiency of an X-ray tube, or the ratio of the energy of the X-rays to that of the cathode rays, is represented, to a first approximation at least, by an equation of the type

$$\rho = CNV,$$

where  $C$  is a constant,  $N$  the atomic number, and  $V$  the applied voltage. The numerical value of the efficiency is even to-day very small and of the order of one-thousandth. Nevertheless, as the energy of the cathode rays may be very large (several kilowatts) the energy radiated as X-rays is still important.

### 5. Properties of the radiation emitted in various directions.

**. . . Polarisation of X-rays.**—Some aspects of the problem of the emission from an anticathode bombarded by electrons have just been considered. A general question and one of great interest consists in ascertaining exactly what are the intensity, the composition, and the state of polarisation of

the radiation emitted in various azimuths round the anti-cathode serving as the source of the rays. Some account will be given of the investigations which have been undertaken to elucidate these different points.

If only one atom were struck by a corpuscle moving with a given velocity the direction of this velocity would obviously be an axis of symmetry of the phenomenon. In addition, the properties of the wave emitted according to the classical electromagnetic theory when an electron is stopped by matter could be visualised by means of the Stokes-Wiechert-Thomson theory, if it were assumed that

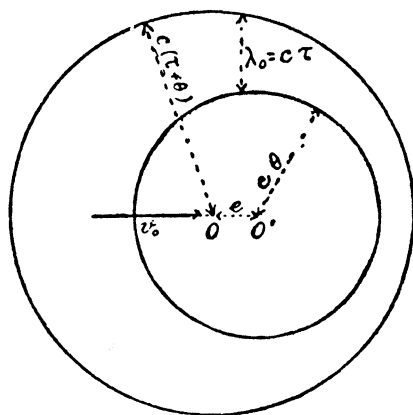


FIG. 11.

the path during the stoppage was a straight line, the prolongation of the direction of the velocity of the corpuscle, and if the retardation were uniform.

For example, if the electron is stopped in the distance,  $l = OO'$  (Fig. 11), the time of stoppage being  $\tau$  such that

$$\tau = \frac{v_0}{\gamma} = \frac{2l}{v_0},$$

the energy of the wave at the time,  $\tau + \theta$  will be confined between two spheres with centres at O and O'. Inside the sphere centre O' there will be only the static field of the electron and the disturbance due to the stoppage will not have

spread beyond the sphere O. The greater the acceleration, the nearer together will be the spheres, and if  $\lambda_0$  be their separation in the direction normal to  $OO'$ , then

$$\lambda_0 = c\tau = \frac{2lc}{v_0}.$$

Several important consequences can be deduced from this theory; they provide at least an indication of what could be predicted for the properties of the emitted wave if it were possible to admit the very simple hypotheses on which the theory is based.

(1) According to the classical electromagnetic theory the wave is entirely polarised. As the plane of polarisation, in the usual sense of the term, is normal to the electric vector, it will be perpendicular to the plane which contains the radius  $OP$  and the direction  $OV$  of the velocity of the cathode rays.

(2) The intensity of the wave varies with the angle which  $OP$  makes with  $OV$ ; it is zero when these two lines coincide and becomes a maximum when they are at right angles.

(3) The distance between the two spherical surfaces varies with the azimuth; the smaller it is the more rapid will be the variation of the field and the more will the properties of this impulse wave resemble those of a radiation of short wave-length. In this way the variation of the penetration of the X-rays with the angle between the direction of emission and the cathode rays could be foreseen. The wave-length  $\lambda_\phi$  for an angle  $\phi$  is given by

$$\lambda_\phi = l\left(\frac{2c}{v_0} - \cos \phi\right)$$

which indicates some analogy with Döppler's phenomenon.

At the present time it is quite certain that the conditions of emission are very different from those which correspond to the preceding case. In the first place, there are characteristic radiations due to the fluorescence of the anticathode which can have no connection with the original direction of the exciting corpuscles. Also there is no doubt that the continuous spectrum itself is governed by the laws of quanta

which are ignored by the electromagnetic theory. Finally, we know almost nothing concerning the conditions of the stoppage of the electrons by a solid body. Nevertheless, the foregoing conclusions are justified by experiment up to a certain point.

*Polarisation.*—After investigations by Röntgen [21], Walter [22] and Bassler [23], Barkla [24] was able to discover a partial polarisation of the radiation.

Unfortunately, no instruments are known which are capable of acting as analysers in the case of X-rays as do well-known pieces of apparatus in luminous optics. Differences of polarisation can only be recognised (more or less effectively) by having recourse to the re-emission by scattering.

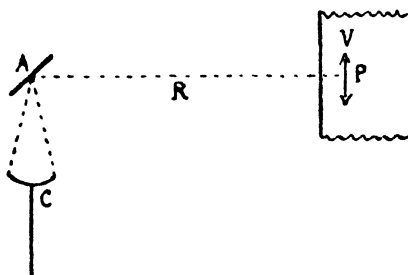


FIG. 12.

Suppose a beam of cathode rays CA is incident on the anticathode A (Fig. 12), and consider the electric vector of the wave, the preceding theory being admitted. It will lie in the plane of the figure and for a ray ARP will be perpendicular to AP. If there is a secondary radiator at P the electrons of the atoms of this radiator will enter into forced vibrations along PV, under the influence of the primary radiation, and these secondary vibrations will behave as a source of polarised light. This relates to the secondary X-rays produced by scattering and not to the characteristic fluorescent rays from P.

If an ionisation chamber is placed in the plane at right-angles to the plane of the figure and containing PV it can

be ascertained whether, as these considerations indicate, the radiation from P is polarised; for example, whether the energy emitted in the direction of vibration shows a more or less marked minimum. In Barkla's apparatus the tube AC could be turned in the plane perpendicular to the figure and through AC, which made PV turn in the plane containing the ionisation chamber, and thus the connection of the ionisation observed with the polarisation expected could be verified.

Barkla's results, extended and confirmed by those of Haga, Herweg, Bassler and Vegard [25], have shown that there is a partial polarisation (10 to 20 per cent.) in a direction in accordance with the theory.

Up to the present, the phenomena of the polarisation of X-rays have remained rather isolated on account of the only partial nature of the polarisation and also on account of the difficulty attending their investigation. If a suitable analyser for high-frequency radiations could be discovered much progress could doubtless be made. The explanation of the Stark effect by the quantum theory has shown that polarised waves can be predicted and explained otherwise than by assuming the pure electromagnetic theory.

The more recent experiments of Kirkpatrick [67] would appear to indicate that the state of polarisation of the rays emitted by a tube is more marked towards the short wave-lengths; but even for rays of wave-length  $0.3 \text{ \AA}$ . the degree of polarisation (ratio of the two components of the radiation) does not exceed 0.835.

But polarisation is not the only phenomenon which has been found to cause a dissymmetry in the radiation from an anticathode in different directions. The intensity and the penetrating power of the rays are found to vary with the azimuth.

*The variation of the intensity and the quality of the rays with the azimuth.*—Kaye [26] and Stark [27] have discovered the principal feature of this variation by studying the radiation emitted by anticathodes formed of very thin sheets of

different elements (aluminium, copper, platinum, and gold) or of a greater thickness of a light element such as carbon.

In the case of a thin sheet, the radiation emerging in the direction of the cathode rays (azimuth  $0^\circ$ ) is more intense than that which returns along the path of these rays (azimuth,  $180^\circ$ ). The ratio may even reach 3 : 1 and increases with the energy of the cathode rays. Kaye also found that, in general, the radiation was more penetrating in the former direction than in the latter, which agrees with the relation of the Döppler type on page 93, and Stark reached the same conclusion.

The investigations of Loebe, Ham, Miller, Friedrich, Kirchbaum [28], although they show some differences, on

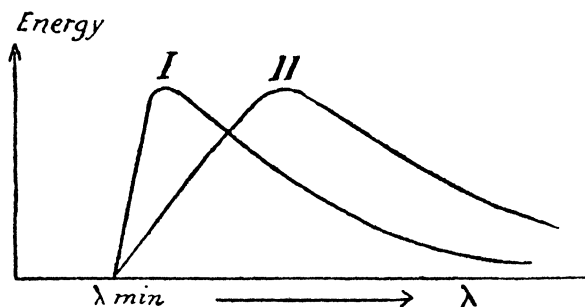


FIG. 13.

the whole confirm the first results of Kaye and Stark. The interpretation of the experimental data is simpler in the case of experiments made with thin anticathodes.

The fact that the penetration of the emitted radiations varies with the azimuth gives rise to an important question concerning the high-frequency limit of the continuous spectrum emitted at a constant potential and the value of  $h$  deduced therefrom.

Is this limit of the continuous spectrum independent of the azimuth? If not, the measurements of  $h$  will be gravely affected. Wagner [29], in particular, has attacked this problem and gives the curves shown in Fig. 13 for the distribution of the energies in the two azimuths  $0^\circ$  and  $150^\circ$ . As



will be seen, the lower limit of wave-length is the same and the measurements of  $h$  remain good, but the trend of the curve II explains the lower penetration of the radiation in the azimuth of  $180^\circ$ .

Fig. 14 also relates to measurements by Wagner of the radiation in azimuths of  $90^\circ$  and  $150^\circ$ .

Wien had predicted theoretically that for an applied voltage of 8000 volts a difference of 800 volts should be found between the two azimuths mentioned, if X-rays could be considered as waves due to the acceleration of electrons. Wagner having found nothing like this with a voltage of this order, Stokes' theory is proved to be insufficient; but

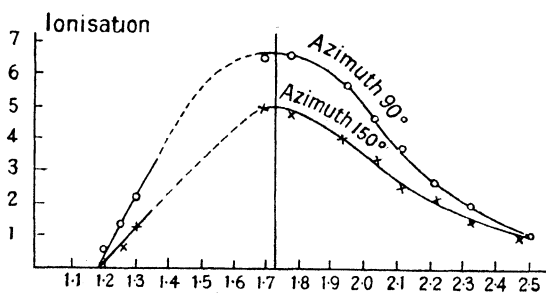


FIG. 14.

if this theory is rejected, an explanation on the quantum theory must be found of the variation of the penetration which the pure electromagnetic theory explains so well.

If energy has inertia it must also possess momentum; the application of the conservation of momentum to the system matter-energy then leads to a prediction of a result such as has been observed. This applies to all theories assuming these two principles.

## PART II

### LINE SPECTRA

**1. The emission of characteristic lines.**—In addition to the continuous spectrum a tube emits rays characteristic

of its anticathode. Before the diffraction of X-rays was known, Whiddington and Beatty [30] had been able to show that when an anticathode was bombarded by cathode rays of increasing velocity, sudden changes in the intensity and in the nature of the emitted radiation were produced at certain critical velocities. These changes corresponded to the appearance of fluorescent X-rays about which, even at that time, much was known owing to Barkla's work. Whiddington's numerical results had already very clearly demonstrated the existence of a relation between the energy of the cathode rays and the penetrating power (frequency) of the excited radiations.

Webster [31] has pursued the investigation of the excitation of the characteristic rays by means of the methods which have been described in the first part of this chapter (p. 84), that is to say, he has drawn the spectral and isochromatic curves for the intensities of the rays emitted by a tube capable of being worked at various well-defined voltages, and thus with cathode rays which had definite velocities when they reached the anticathode.

A first series of investigations was on the K series of rhodium and led to the four following laws :—

(1) When the potential applied to the tube is increased, all the K lines appear together at the same critical potential.

(2) This critical potential is connected with the frequency of the K absorption discontinuity of rhodium by the quantum relation.

(3) When the potential is further increased, the intensity of these lines increases rapidly without their relative intensities being appreciably modified.

(4) The curve showing the intensities of the lines as a function of the potential is concave upwards whilst the corresponding curve for the general radiation is at first concave downwards and then nearly straight.

Hull and Rice, and afterwards Wooten, found similar results for tungsten, palladium and molybdenum.

It is important to emphasise the difference which is

presented between the excitation of the continuous spectrum and that of the characteristic lines. Let us consider, for example, the K lines of an element standing out from a continuous background as in Fig. 6, and let us suppose that the potential applied to the tube is gradually increased in such a way that the limit of the continuous spectrum (which corresponds to the quantum of the cathode rays) is at first on the right of  $K\alpha_2$  and moves towards the left, to the high-frequency side. When we arrive at a certain line  $\alpha_1$ , for example, the radiation of the continuous spectrum having this frequency will be excited but the line will not,

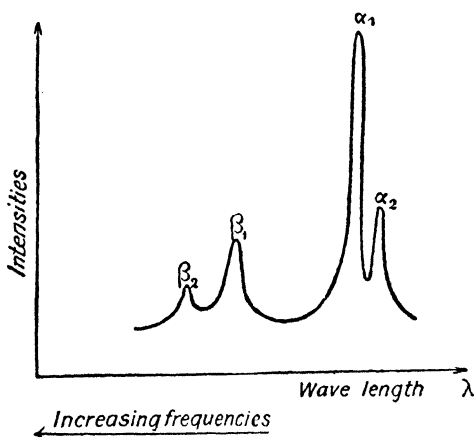


FIG. 15.

and this state of affairs will continue till the limit of the continuous spectrum reaches the absorption discontinuity of the element considered ; all the lines belonging to the K series will then be excited.

Bohr's theory agrees very well with these results, since, in order to excite the K series, it is necessary to have occasioned an empty place on the K level, i.e. to have employed a radiation, corpuscular or undulatory, the former in this case, which has a quantum large enough to penetrate, so to speak, to the K level.

*The excitation of the lines of the L series,—Webster and*

Clark [32] carried out an investigation on the L series of platinum similar to that on the K series of rhodium, and discovered two critical potentials corresponding to the two discontinuities  $L_1$  and  $L_2$  which are found in the L absorption spectra of the elements. It is extremely probable that the  $L_3$  discontinuity acts in the same way though it is more difficult to establish this fact on account of its close proximity to  $L_2$ .

Thus, it is possible by adjusting the potential applied to the tube so that it is between the values which correspond to the quanta of the  $L_1$  and  $L_2$  discontinuities, to excite only those lines of the L series which are connected with the  $L_1$  level (i.e. those which involve the arrival of an electron at this level).

The lines corresponding to the  $L_2$  level will also appear if the potential is increased beyond that corresponding to the  $L_2$  quantum.

The multiple structure of the L series can be demonstrated in this way and each of the lines can be assigned to the level,  $L_1$ ,  $L_2$ , or  $L_3$ , with which it is connected. Webster only examined the strongest lines; A. Dauvillier [33] has been able to extend this method of investigation to the numerous very weak lines of the L series, and has obtained the distribution of the lines between the levels which is given in Table XXVB.

## 2. The intensity of emission of characteristic lines.—

Webster [31] has studied the emission of the K lines of rhodium. It has been mentioned (p. 98) that the whole series is excited when the applied voltage passes a certain critical value  $V_0$ . At this and higher potentials,  $V$ , he has found that the intensity of each line increases proportionally to  $(V - V_0)^{\frac{3}{2}}$ . He has also verified this law for the L lines of platinum.

Wooten [34] has investigated the emission of the K lines of molybdenum and palladium. His results give a variation of the intensities proportional to  $V^2$  rather than to  $(V - V_0)^{\frac{3}{2}}$ ; the question thus calls for further research.\*

\* See the more recent work of Keltmann, *Zeits. für Phys.*, 1923, 18, 6.

Few measurements have been made of the ratios of the intensities of different lines. This ratio, however, is very different inside and outside the tube, even for lines which are close together, on account of the rapid variation with the wave-length of the coefficient of absorption of the walls of the tube.

Taking this into account, Wooten has found that the ratio of the intensity of the  $\alpha$  doublet to that of the  $\beta$  line has the value 5.55 for molybdenum and 6.25 for palladium.

It follows from the foregoing data that in the complex spectrum composed of lines superposed on a continuous background, which is emitted by ordinary tubes, the relative intensities of the lines and the continuous spectrum vary with the voltage, the intensity of the lines increasing more rapidly than that of the continuous spectrum.

Bergen Davis [11] has proposed a theory to account for the energy of emission of the lines.

It is seen that this part of the study of X-rays has been only very incompletely attacked so far. It is, however, made difficult by the obstacles which arise in the conversion of the experimental ionisation curves to the true distribution of the emission intensities inside the tube. Nevertheless, the problems which it raises are of very great importance, and it is most desirable that new experimental investigations should be made in this direction.

It is all connected with the still unsolved problem of the conditions under which electrons are stopped and retarded when they penetrate into solid screens.

### **DATA CONCERNING THE LINES OF THE VARIOUS SERIES FOR ALL THE ELEMENTS**

The high-frequency spectra of the elements have the remarkable characteristic of being, so to speak, constructed in the same manner. It has already been stated, concerning the absorption discontinuities, that all the elements possess critical absorption frequencies which vary from one

substance to another according to Moseley's law. For each element the first discontinuity, designated by the letter K, is single and corresponds to a single quantum ; the second, or L discontinuity, is triple and corresponds to two quanta ; the third, or M discontinuity, is still more complex and corresponds to three quanta, and so on.

The lines, which can be deduced from the discontinuities by the principle of combination, will therefore have an analogous structure throughout the series of the elements and will resolve themselves into natural groups, K, L, M, . . . , each discontinuity being connected with a series of lines which all appear at once.

**3. Lines of the K series.**—The lines of the K series are known from the heavy elements down to sodium ( $N = 11$ ).

For the elements of high atomic weight the K series is composed of four lines. There is first a doublet  $\alpha_1\alpha_2$  which has its origin in the two levels  $L_1, L_2$  of the L series, and shows a frequency difference throughout the series of the elements which conforms to Sommerfeld's law.\* It is a regular doublet characterised by

$$\Delta\lambda = \text{constant.}$$

The stronger of the  $\alpha$  lines is  $\alpha_1$ , which is of higher frequency than  $\alpha_2$ . Then comes the  $\beta$  line, attributed to one of the M levels, and then the  $\gamma$  line, arising from an N level (sometimes the  $\beta$  and  $\gamma$  lines are called  $\beta_1$  and  $\beta_2$ ).

The K spectrum of tungsten has been examined in detail and its lines, nowadays well known, have the wave-lengths given in Table XVII. Actually the  $\beta$  line is a close doublet, the component of greater wave-length being the weaker (de Broglie [35]), the difference being

$$\Delta\lambda = 0.0007 \text{ \AA.}$$

This satellite of the  $\beta$  line has been observed for platinum

\* See Siegbahn, "Accurate Measurements of the Copper Lines," *Phil. Mag.*, 1919; de Broglie, *Comptes Rendus*, 1919, 2, p. 962; Duane and Patterson, *Nat. Acad. Sci. Proc.*, 1920, p. 516.

## LINE SPECTRA

and rhodium and by Duane for molybdenum. It will be seen later that the K series is complex for all elements of low atomic weight. This group  $\beta_1\beta'_1$  is a regular doublet.

Duane and Stenström [36] have announced another line  $\alpha_3$  which would be that of greatest wave-length for the group, and would proceed from the  $L_3$  level. In fact, there should be as many  $\alpha$  lines in the K series as there are L discontinuities.

The platinum lines have also been determined though not with such great accuracy (Table XVIII).

TABLE XVII  
WAVE-LENGTHS OF THE LINES OF THE K SERIES OF TUNGSTEN  
(Ångström Units)

PHOTOGRAPHIC METHOD. Rock Salt: $d = 2.814 \times 10^{-8}$ cm. Calcite: $d = 3.02904 \times 10^{-8}$ cm.				IONISATION METHOD. Calcite: $d = 3.028 \times 10^{-8}$ cm.	
Lines.	Ledoux-Lebard and Dauvillier.	Dershem.	Siegbahn.	Duane and Shimizu.	Duane and Stenström.
$\alpha_2$ . . . .	0.2128	0.2124	0.21352	0.2134	0.21341
$\alpha_1$ . . . .	0.2053	0.2076	0.20885	0.2087	0.20860
$\beta$ . . . . .	0.1826	0.1834	0.18436	0.1842	0.18420
$\gamma$ . . . . .	0.1768	0.1784	0.17940	—	0.17901
Absorption dis- continuity .	—	—	—	0.1785	0.17806

TABLE XVIII  
WAVE-LENGTHS OF THE LINES OF THE K SERIES OF PLATINUM  
(Ångström Units)

Lines.	Rogers.	Seemann and Lilienfeld.	De Broglie.
$K\alpha_2$ . . . .	$0.1895 \pm 2$	0.191	0.1898
$K\alpha_1$ . . . .	$0.1851 \pm 1$	0.185	0.1850
$K\beta_1$ . . . .	$0.1644 \pm 2$	0.164	0.1634
$K\beta_2$ . . . .	—	0.159	0.1574

Although the K discontinuities are known up to uranium, the measurements and even the identification of the K lines are wanting for elements of atomic weight greater than that of platinum ( $N = 78$ ).

From the rare earths ( $N = 72$ ) down to zinc ( $N = 30$ ) the four principal K lines have been measured, but the measurements which have to be made near the end of the X-ray spectrum are not in all cases as accurate as is necessary. In particular, they do not always agree with the absorption limits, which certainly denotes experimental error.

The K lines of the elements from copper to sodium have been accurately measured by Hjalmar ; Table XIX, completed by the recent measurements of Dolejšek, shows the increasing complexity of the K spectra of the light elements.

Already for copper the K spectrum consists of about ten

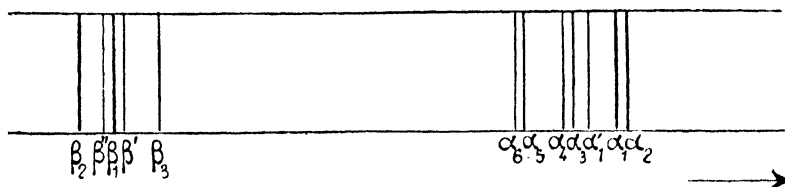


FIG. 16.

components (Dauvillier). It is probable that the appearance of new lines is due to the coming into play of levels which do not contain electrons in the normal state of the atom. These lines are comparable with the lines in the spark spectrum in the case of luminous rays.

According to Hjalmar Fig. 16 represents the complete spectrum of the K series.

Tables XIXA and XX give the whole of the K series. Fig. 4 of Plate 2 refers to the K lines of rhodium and furnishes a characteristic example of the series. In Fig. 6 of Plate 2 the K spectrum of a light element is reproduced (M. Siegbahn's laboratory).

The K series of hydrogen falls in the luminous region of the spectrum and corresponds to the ultra-violet series in the spectrum of this gas.



TABLE XIX

THE K SERIES FOR THE LIGHT ELEMENTS: WAVE-LENGTHS IN ANGSTROM UNITS

Rock Salt:  $d = 2.814 \cdot 10^{-8}$  cm.

Calcite:  $d = 3.0290 \cdot 10^{-8}$  cm.

Elements.	$\alpha_1$	$(\alpha_1 \alpha_2)$	$\alpha'_1$	$\alpha_3$	$\alpha_4$	$\alpha_5$	$\alpha_6$	$\beta_3$	$\beta'$	$\beta_1$	$\beta''$	$\beta_2$
11 Na	—	118836	11835	118024	117814	—	—	—	—	11591	—	—
12 Mg	—	986775	98265	979940	978620	97302	97118	9647	—	953450	—	—
13 Al	—	831940	828500	820460	825300	820580	818920	8025	—	794050	—	—
14 Si	—	710917	7083	706382	703372	7014	7003	67933	—	673933	—	—
15 P	—	614171	—	610219	609500	—	—	58202	—	575913	—	—
16 S	536128	536036	—	532833	532175	5277	—	50447	—	501913	—	—
17 Cl	471821	—	4712	4688	4684	—	—	44000	—	439450	4391	—
19 K	373368	—	3730	37110	37088	—	—	—	—	344638	344270	—
20 Ca	335169	—	3349	33323	33300	—	—	—	—	308297	307957	306740
21 Sc	302503	—	3023	$\left. \begin{array}{l} 3006 \\ 27269 \\ 2486 \\ 22733 \\ 20879 \\ 19233 \\ 17774 \\ 16476 \\ 153075 \\ 14288 \end{array} \right\}$			—	—	—	—	—	—
22 Ti	274317	—	—	—	—	—	—	—	—	277366	—	2755(5)
23 Va	249835	—	—	—	—	—	—	—	—	250874	—	249367
24 Cr	228484	—	—	—	—	—	—	—	—	227968	—	226537
25 Mn	209732	—	—	—	—	—	—	—	—	2079	—	—
26 Fe	193230	—	—	—	—	—	—	—	—	1907	—	—
27 Co	178528	—	—	—	—	—	—	—	—	175884	—	—
28 Ni	165461	—	—	—	—	—	—	—	—	175397	—	—
29 Cu	—	—	—	—	—	—	—	—	—	161715	—	1606
30 Zn	143206	—	—	—	—	—	—	—	—	149669	—	148303
				153075	14288	—	—	—	—	138887	—	1382
				—	—	—	—	—	—	129271	—	—

References.—Siegbahn, *Phil. Mag.*, June, 1919, p. 601; Nov., 1919, p. 647. Hjalmar, *Zeits. f. Physik*, 1920, 1, 5, p. 439.  
Dolejssek, *Comptes Rendus*, 13 Feb., 1922. Stenstrom, Stenstrom (extract from the Bulletin of the National Research Council,  
Nov., 1920). Siegbahn and Dolejssek, *Zeits. f. Physik*, 1922, 10, p. 159.

TABLE XIXA  
WAVE-LENGTHS OF THE LINES OF THE K SERIES FROM SODIUM TO ZINC. (ÅNGSTRÖM UNITS)  
According to Hjalmar, Stensson, Stenström, Siegbahn, Dolejsk

Elements.	$\alpha_1\alpha_2$	$\alpha'_1$	$\alpha_3$	$\alpha_4$	$\alpha_5$	$\alpha_6$	$\beta'$	$\beta_1$	$\beta_2$	$\gamma_1$
11 Na	11'8836	11'835	11'8024	11'7814	—	—	—	—	11'591	—
12 Mg	9'86775	9'8265	9'79940	9'78620	9'7302	9'7118	9'647	9'53450	—	—
13 Al	8'31940	8'28560	8'26460	8'25300	8'20580	8'18920	8'025	7'94050	—	—
14 Si	7'10917	7'083	7'06382	7'05372	7'014	7'003	6'7933	6'73933	—	—
15 P	6'14171	—	6'10219	6'09500	—	—	5'8204	5'78513	—	—
	$\alpha_2$	$\alpha'_1$	$\alpha'_1$	$(\alpha_3\alpha_4)$	$\beta'$	$\beta_1$	$\beta''$	$\beta_2$		
16 S	—	—	—	$\alpha_3$ 5'32937 $\alpha_4$ 5'32325	—	—	—	—	—	—
17 Cl	5'36375	5'36090	5'3406	4'686	5'047	5'0213	4'39080	5'0128	—	—
19 K	4'72185	4'71870	—	3'710	—	4'39450	3'44290	—	—	—
20 Ca	3'73725	3'73386	3'7187	3'331	3'0911	3'44638	3'07957	3'06740	—	—
21 Sc	3'35512	3'35186	3'33986	3'006	2'7992	3'08297	—	2'7555	—	—
22 Ti	3'02863	3'02526	—	2'7269	2'51506	2'77366	—	2'49367	—	—
23 Va	2'74648	2'74284	—	2'4846	2'28526	2'50874	—	2'26537	—	—
24 Cr	2'50212	2'49834	—	2'2733	2'0857	2'27968	—	—	—	2'2646
25 Mn	2'28958	2'28547	—	2'0879	1'9105	—	—	—	—	2'0670
26 Fe	—	2'09777	—	1'9233	1'73560	—	—	—	—	1'8932
27 Co	1'93660	1'93239	—	1'7774	1'6197	1'75272	—	1'74076	1'7402	1'6054
28 Ni	1'79006	1'78578	—	1'6476	1'4990	1'61715	—	1'606	1'48403	1'4854
29 Cu	1'65860	1'65467	—	1'5308	—	1'49669	—	1'3774	1'3780	1'3780
30 Zn	1'54122	1'53736	—	1'4288	—	1'38887	—	1'27915	1'2811	1'2811

TABLE XX

WAVE-LENGTHS OF THE LINES OF THE K SERIES FROM ZINC TO PLATINUM

Measurements already old except for Zn, As, Mo, Rh, Pd, Ag, Cd, Sn \*

Element.	Atomic Number.	$\alpha_2$ .	$\alpha_1$ .	$\alpha_3$ .	$\alpha_4$ .	$\beta_1$ .	$\beta_2$ .
Zinc . . .	30	1'43598	1'43205	—	—	1'29268	1'281
Gallium . .	31	1'34161	1'33785	—	—	1'20591	—
Germanium .	32	1'261	1'257	—	—	1'131	1'121
Arsenic . .	33	1'17749	1'17345	—	—	1'052	1'039
Selenium . .	34	1'109	1'104	—	—	0'993	—
Bromine . .	35	1'040	1'035	—	—	0'929	0'914
Rubidium . .	37	0'926	0'922	—	—	0'825	0'813
Strontium . .	38	0'876	0'871	—	—	0'779	0'767
Yttrium . .	39	0'840	0'835	—	—	0'746	0'733
Zirconium . .	40	0'793	0'788	—	—	0'705	—
Niobium . .	41	0'754	0'749	—	—	0'669	0'657
Molybdenum .	42	0'71196	0'70759	—	—	0'63065	0'61938
Ruthenium . .	44	—	0'645	—	—	0'574	—
Rhodium . .	45	0'61656	0'61232	—	—	0'5440	0'5342
Palladium . .	46	0'58850	0'58421	—	—	0'51962	0'51021
Silver . . .	47	0'56257	0'55816	—	—	0'49597	—
Cadmium . .	48	0'53831	0'53395	—	—	0'47414	0'4647
Indium . . .	49	0'515	0'510	—	—	0'453	0'440
Tin . . . .	50	0'49385	0'48947	—	—	0'432	—
Antimony . .	51	0'472	0'468	—	—	0'416	0'408
Tellurium . .	52	—	0'456	—	—	0'404	—
Iodine . . .	53	—	0'437	—	—	0'388	—
Caesium . .	55	0'402	0'398	—	—	0'352	—
Barium . . .	56	0'393	0'388	—	—	0'343	—
Lanthanum . .	57	0'376	0'372	—	—	0'329	—
Cerium . . .	58	0'360	0'355	—	—	0'314	—
Praseodymium .	59	0'347	0'342	—	—	0'301	—
Neodymium . .	60	0'335	0'330	—	—	0'292	—
Tungsten . .	74	0'21341	0'20860	—	—	0'18420	0'17901
Platinum . .	78	0'1898	0'1850	—	—	0'1634	0'1574

**4. Lines of the L series.**—The L series was quickly found to be very complex. It is known that the L group is actually triple, resulting from the existence of three L absorption levels,  $L_1$ ,  $L_2$ ,  $L_3$ , each giving rise to its own particular group of lines. Table XXVB, compiled from Dauvillier's

\* Measurements of A. Leide (M. Siegbahn, *Jahrbuch der radioaktivitat und Elektronik*, 1922, p. 276); the old measurements are given with only three decimal places (Å.U.); the measurements for gallium are due to Uhler and Cooksey.

TABLE

## WAVE-LENGTHS OF THE L LINES FROM

The 4th and 5th decimal places are stated by the authors  
of Ruthenium and the  $\eta$ ,

Element.	Atomic Number.	$L$ .	$a_2$ .	$a_1$ .	$a_3$ .	$\eta$ .	$\beta_4$ .
Zinc . . . . .	30	—	—	12'346	—	—	—
Arsenic . . . . .	33	—	—	9'701	—	—	—
Bromine . . . . .	35	—	—	8'391	—	—	—
Rubidium . . . . .	37	—	—	7'335	8'360	—	—
Strontium . . . . .	38	—	—	6'879	—	—	—
Yttrium . . . . .	39	—	—	6'464	6'440	—	—
Zirconium . . . . .	40	—	—	6'083	6'057	—	—
Niobium . . . . .	41	—	5'731	5'724	5'709	—	—
Molybdenum . . . . .	42	—	5'410	5'403	5'381	—	—
Ruthenium . . . . .	44	—	4'853	4'83567	4'823	—	—
Rhodium . . . . .	45	—	—	4'58778	4'577	—	—
Palladium . . . . .	46	—	4'374	4'35850	4'352	—	4'071
Silver . . . . .	47	—	4'155	4'14564	4'133	—	3'861
Cadmium . . . . .	48	—	3'959	3'94782	—	—	3'676
Indium . . . . .	49	—	3'774	3'76367	—	—	—
Tin . . . . .	50	—	3'604	3'59193	—	—	3'337
Antimony . . . . .	51	—	3'443	3'43177	—	—	3'184
Tellurium . . . . .	52	—	3'299	3'28169	—	—	3'044
Iodine . . . . .	53	—	3'155	3'14136	—	—	2'911
Caesium . . . . .	55	—	2'899	2'88587	—	—	2'668
Barium . . . . .	56	—	2'786	2'76931	—	—	2'558
Lanthanum . . . . .	57	—	2'674	2'65931	—	—	2'453
Cerium . . . . .	58	—	2'573	2'55559	—	—	2'357
Praseodymium . . . . .	59	—	2'472	2'45735	—	—	—
Neodymium . . . . .	60	—	2'379	2'36494	—	—	2'167
Samarium . . . . .	62	—	2'210	2'200	—	—	—
Europium . . . . .	63	—	2'131	2'121	—	—	1'923
Gadolinium . . . . .	64	—	2'054	2'043	—	—	1'851
Terbium . . . . .	65	—	1'983	1'973	—	1'935	1'784
Dysprosium . . . . .	66	—	1'916	1'907	—	—	1'721
Holmium . . . . .	67	—	1'854	1'843	—	—	1'657
Erbium . . . . .	68	—	1'794	1'783	—	1'725	1'599
Ytterbium . . . . .	70	1'892	1'681	1'670	—	1'618	1'490
Lutecium . . . . .	71	1'834	1'629	1'619	—	—	1'437
Tantalum . . . . .	73	—	1'528	1'518	—	1'435	1'343
Tungsten . . . . .	74	1'67505	1'48452	1'47348	—	1'4177	1'29874
Osmium . . . . .	76	—	1'398	1'388	—	—	1'214
Iridium . . . . .	77	—	1'360	1'350	—	—	1'176
Platinum . . . . .	78	1'499	1'323	1'313	—	1'242	1'142
Gold . . . . .	79	1'457	1'283	1'271	—	1'197	1'102
Mercury . . . . .	80	—	1'251	1'240	—	—	—
Thallium . . . . .	81	1'385	1'215	1'205	—	1'124	1'036
Lead . . . . .	82	1'348	1'186	1'175	—	1'091	1'008
Bismuth . . . . .	83	1'317	1'153	1'144	—	1'059	0'977
Polonium . . . . .	84	—	—	1'101	—	—	—
Radium . . . . .	88	—	—	1'010	—	—	—
Thorium . . . . .	90	1'117	0'969	0'957	—	—	—
Uranium . . . . .	92	1'066	0'922	0'911	—	—	—

## XXI

ZINC TO URANIUM. (ÅNGSTRÖM UNITS)

to be less certain except in the case of the  $\alpha_1$  and  $\gamma_1$  lines  
 $\beta_2$  and  $\gamma_2$  of Tungsten

$\beta_1$ .	$\beta_2$ .	$\beta_3$ .	$\beta_4$ .	$\gamma_1$ .	$\gamma_2$ .	$\gamma_3$ .	$\gamma_4$ .
—	—	—	—	—	—	—	—
9'449	—	—	—	—	—	—	—
8'141	—	—	—	—	—	—	—
7'091	—	—	—	—	—	—	—
6'639	—	—	—	—	—	—	—
6'227	—	—	—	—	—	—	—
5'851	—	—	—	5'386	—	—	—
5'493	5'317	—	—	—	—	—	—
5'175	—	—	—	—	—	—	—
4'61100	—	—	—	4'17282	—	—	—
4'36490	—	—	—	3'93570	—	—	—
4'13730	3'904	4'030	—	3'71636	3'597	—	—
3'92664	3'698	3'823	—	3'51485	—	—	—
3'73008	3'514	3'639	—	3'32800	—	—	—
3'54783	3'354	—	—	3'15529	—	—	—
3'37762	3'172	3'300	—	2'99460	2'903	2'889	2'831
3'21836	3'021	3'149	—	2'84507	2'782	—	—
3'06964	2'881	3'007	—	2'70613	—	—	—
2'93066	2'750	2'873	—	2'57712	—	—	—
2'67750	2'514	2'629	—	2'35950	2'234	—	—
2'56224	2'407	2'520	—	2'23625	—	—	—
2'45294	2'307	2'414	—	2'13680	—	—	—
2'35061	2'212	2'307	—	2'04400	2'003	—	—
2'25353	2'120	2'217	—	1'95641	1'937	1'933	—
2'167	2'036	2'128	—	1'83743	1'803	1'775	—
1'99317	1'884	1'965	—	1'725	1'659	—	—
1'918	1'810	1'888	—	1'662	1'599	1'590	—
1'844	1'744	1'811	—	1'597	(1'562)	(1'558)	—
1'775	1'682	1'745	1'659	1'531	1'477	1'470	1'437
1'709	1'622	1'683	—	1'470	1'422	1'418	—
1'646	1'568	1'620	—	1'415	1'369	1'365	—
1'586	1'514	1'560	—	1'367	1'323	1'316	—
1'474	1'414	1'451	1'422	1'267	1'228	1'223	—
1'421	1'368	1'399	—	1'224	1'188	1'183	—
1'323	1'280	1'303	—	1'135	1'101	1'097	—
1'27917	1'24191	1'26000	1'2031	1'09553	1'06584	1'05965	1'02647
1'194	1'167	1'176	—	1'021	—	—	—
1'154	1'133	1'138	1'101	0'989	0'962	0'956	0'917
1'120	1'101	1'098	1'072	0'958	0'933	0'929	0'900
1'080	1'065	1'059	1'035	0'922	0'898	0'894	0'869
1'049	1'042	—	—	0'896	—	—	—
1'012	1'006	0'998	0'977	0'864	0'844	0'840	0'808
0'983	0'983	0'968	—	0'842	0'820	0'816	0'792
0'950	0'954	0'937	0'923	0'810	0'794	0'790	0'762
0'920	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
0'766	0'797	0'758	—	0'654	0'635	—	—
0'720	0'756	0'710	—	0'615	0'596	—	—

measurements,\* shows how the lines have been assigned to the various levels. So far about thirty L lines have been measured and the number is constantly increasing. On account of the difference between the paths of the Moseley curves for the three L levels the groups of lines which correspond to them overlap at certain points, and this slightly modifies the general aspect of the spectra. For example, the  $\alpha$  and  $\gamma$  groups of the L spectra of platinum and tungsten can easily be distinguished in Fig. 3 of Plate 2 whilst the configuration of the  $\beta$  groups is changed.

For elements of fairly low atomic weight (below antimony,  $N = 51$ ), the number of intense L lines diminishes and the series appears to become less complex. The values of the wave-lengths of the lines of the L series which have been measured from uranium (92) to zinc (30) are given in Table XXI.

The investigations of Dauvillier and of Coster have shown that  $\gamma_2$  and  $\beta_5$  disappear at about erbium,  $\gamma_4$  at silver, and  $\gamma_1$  and  $\beta_2$  between zirconium and strontium. This would seem to correspond to the decrease in the number of layers occupied by the electrons in the normal atom as the atomic number decreases.

Millikan [37] has recently discovered the L series in the extreme ultra-violet for elements in the neighbourhood of aluminium ( $N = 13$ ). It is known that Balmer's series can be regarded as the L series of hydrogen.

Tungsten lines are often used for comparison, and the most recent determinations of the wave-lengths of these lines are given in Table XXII.

The wave-lengths of the L lines of the heavy elements are given in Table XXV.

**5. Lines of the M series and of the N series.**—The lines of the M series have wave-lengths of the order of 4 Ångström units even for the very heavy elements, and this makes their investigation difficult; little is known about them. The

\* The  $\beta_5$ ,  $\gamma_2$ , and  $\gamma_4$  lines are very near absorption limits. Their assignment has given rise to some discussion (see Webster [58]).

TABLE XXII

WAVE-LENGTHS OF THE LINES OF THE L SERIES OF TUNGSTEN  
(Ångström Units)

Lines.	ROCK SALT: $d = 2.814 \cdot 10^{-8}$ cm.				CALCITE: $d = 3.028 \cdot 10^{-8}$ cm.	
	Gorton.	Dershem.	Overn.	Siegbahn.	A. H. Compton.	Duane and Patterson.
$l$	—	—	—	1'67505	—	1'6756 $\pm$ 10
$\alpha_2$	1'476	1'4828	1'4839	1'48452	1'4840	1'4839 $\pm$ 3
$\alpha_1$	1'466	1'4722	1'4731	1'47348	1'4728	1'47306 $\pm$ 11
$\eta$	—	1'4163	—	1'4177	—	1'4176 $\pm$ 7
	—	—	—	—	1'3360	—
$\beta_4$	1'292	1'2977	1'2984	1'29874	1'2982	1'2985 $\pm$ 4
	1'283	1'2868	1'2872	1'2871	—	—
$\beta_1$	1'275	1'2784	1'2793	1'27917	1'2787	1'27892 $\pm$ 9
$\beta_3$	1'256	1'2586	1'2598	1'26000	1'2598	1'2601 $\pm$ 3
$\beta_2$	1'237	1'2416	1'2434	1'24191	1'2416	1'24193 $\pm$ 12
	—	—	1'2355	1'2395	—	—
	—	1'2202	1'2212	1'2205	1'2183	—
	—	—	1'2132	1'2118	—	—
	—	1'2098	1'2097	—	—	—
$\beta_5$	—	1'1773	1'2021	1'2031	—	1'2040 $\pm$ 7
	—	1'1292	1'1302	1'1284	—	—
$\gamma_1$	1'094	1'0953	1'0967	1'09553	1'0961	1'09608 $\pm$ 7
	—	—	1'0794	—	—	—
	—	1'0705	1'0724	—	—	—
$\gamma_2$	—	1'0648	1'0659	1'06584	1'0650	1'0655 $\pm$ 4
$\gamma_3$	1'057	1'0587	1'0596	1'05965	1'0580	1'0596 $\pm$ 3
	—	1'0427	1'0446	—	1'0396	—
$\gamma_4$	1'025	1'0253	1'0263	1'02647	1'0247	1'0261 $\pm$ 6

References.—W. S. Gorton, *Phys. Rev.*, Feb., 1916, p. 203; and March, 1916, p. 334. A. H. Compton, *Phys. Rev.*, June, 1916, p. 646. E. Dershem, *Phys. Rev.*, June, 1918, p. 461. O. P. Overn, *Phys. Rev.*, Aug., 1919, p. 137. M. Siegbahn, *Phil. Mag.*, Nov., 1919, p. 639. Duane and Patterson, *Phys. Rev.*, 1920.

lines of this series \* are generally characteristically diffuse, which may indicate a complex structure (Tables XXIII and XXIV).

Dolejsek [51] has lately found and measured approximately some lines belonging to the N series of uranium (between  $\lambda = 8.6$  and  $\lambda = 12.0$  Å.) and thorium (between  $\lambda = 9.4$  and  $\lambda = 13.5$  Å.). Below bismuth the wave-lengths become too great for investigation by crystalline diffraction.

Note.—In a general way the X-ray spectra of the light

\* See Fig. 5, Plate 2.

TABLE XXIII

WAVE-LENGTHS OF THE LINES OF THE M SERIES FROM DYSPROSIUM TO URANIUM. (ÅNGSTRÖM UNITS)

Elements.	Atomic Number.	$\alpha$ .	$\beta$ .	$\gamma$ .	$\delta$ .	$\epsilon$ .
Uranium . . . .	92	3'9014	3'7083	3'4714	2'943	2'813
Thorium . . . .	90	4'1292	3'9333	3'6565	3'127	3'006
Bismuth . . . .	83	5'1072	4'8993	4'5238	—	—
Lead . . . . .	82	5'2751	5'0648	4'6637	—	—
Thallium . . . .	81	5'4499	5'2384	4'802	—	—
Gold . . . . .	79	5'819	5'601	5'115	—	—
Platinum . . . .	78	6'035	5'818	5'295	—	—
Iridium . . . . .	77	6'245	6'029	—	—	—
Osmium . . . . .	76	6'477	6'250	—	—	—
Tungsten . . . .	74	6'976	6'749	6'091	—	—
Tantalum . . . .	73	7'237	7'012	—	—	—
Lutecium . . . .	71	7'818	7'593	—	—	—
Celtium* . . . .	72	7'521	7'286	—	—	—
Ytterbium . . . .	70	8'130	7'898	—	—	—
Erbium . . . . .	68	8'770	8'561	—	—	—
Holmium . . . .	67	9'123	8'930	—	—	—
Dysprosium . . .	66	9'509	9'313	—	—	—

Reference.—Stenström, *Thesis*, Lund, 1919.

TABLE XXIV

WAVE-LENGTHS OF THE LINES OF THE M SERIES (KARCHER'S MEASUREMENTS). (ÅNGSTRÖM UNITS)

Elements.	Atomic Number.	$\alpha_1$ .	$\beta_1$ .	$\beta_3$ .	$\gamma_1$ .	$\gamma_2$ .	$\gamma_3$ .
Bismuth . . . .	83	5'124	4'915	4'604	4'534	3'932	3'840
Lead . . . . .	82	5'290	5'078	—	4'675	4'073	—
Thallium . . . .	81	5'468	5'254	—	—	—	—
Mercury . . . .	80	5'649	5'439	—	—	—	—
Gold . . . . .	79	5'848	5'632	5'446	5'154	4'530	4'439
Platinum . . . .	78	6'049	5'831	5'649	5'329	4'733	4'623

Reference.—J. C. Karcher, *Phys. Rev.*, April, 1920, p. 285.

\* Coster, *Phil. Mag.*, 1923, No. 275, p. 956.



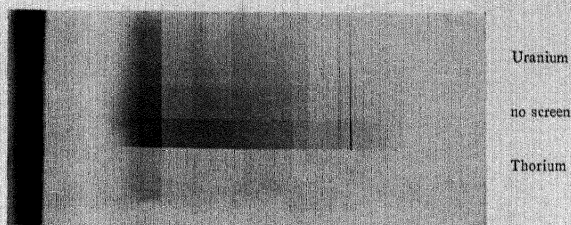


FIG. 1.—THE L ABSORPTION SPECTRA OF URANIUM AND THORIUM

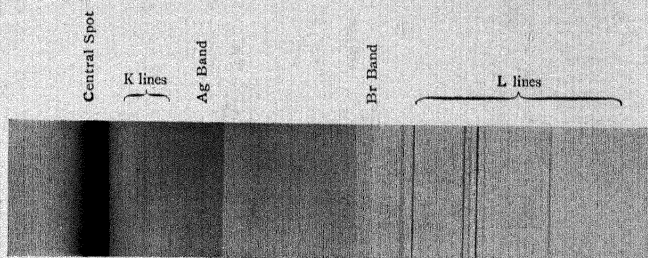


FIG. 2.—THE EMISSION SPECTRUM OF TUNGSTEN

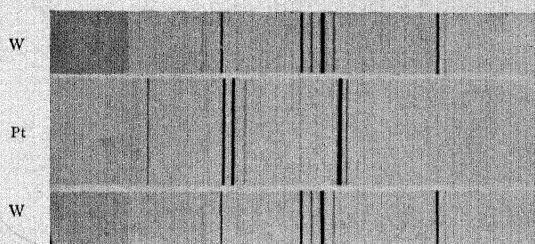


FIG. 3.—MAIN LINES OF THE L SPECTRA OF TUNGSTEN AND PLATINUM

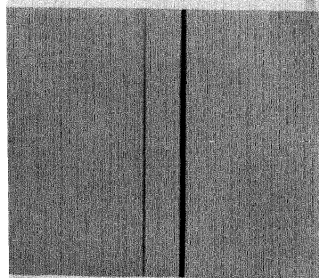
 $\gamma\beta$   $\alpha_1\alpha_2$ 

FIG. 4.—THE K SPECTRUM OF RHODIUM

FIG. 5.—THE M SPECTRUM OF TUNGSTEN  
(Siegbahn)FIG. 6.—THE K SPECTRUM OF ALUMINIUM  
(Siegbahn)



TABLE XXV  
WAVE-LENGTHS OF THE L SERIES OF THE HEAVY ELEMENTS, ACCORDING TO COSTER  
(Angström Units)

Elements.	$\lambda$ .	$\alpha_2$ .	$\alpha_1$ .	$\eta$ .	$\beta_4$ .	$\beta_6$ .	$\beta_1$ .	$\beta_3$ .	$\beta_2$ .	$\beta_5$ .	$\beta_7$ .	$\beta_8$ .
76 Os	—	1'3982	1'38816	—	1'2150	1'2048	1'19459	1'1772	1'16838	—	—	1'140
77 Ir	—	1'35939	1'34834	—	1'1764	1'1717	1'15495	1'1379	1'13287	1'1267	—	1'1030
78 Pt	1'49723	1'32121	1'31008	1'2401	1'1398	1'1317	1'11722	1'09950	1'09050	1'0928	1'0785	1'0701
79 Au	1'45654	1'28489	1'27355	1'1995	1'1044	1'1106	1'08093	—	1'06775	1'0609	1'0465	1'0382
81 Tl	—	1'21603	1'20471	1'125	1'0371	1'0480	1'01266	0'9978	1'00786	—	0'988	0'9783
82 Pb	1'34662	1'18352	1'17202	1'0902	1'00469	1'0188	0'97990	0'96602	0'97990	0'9735	0'9590	0'94952
83 Bi	1'31295	1'1533	1'14115	1'057	0'9754	0'9916	0'94930	0'9357	0'95293	—	—	0'9223
90 Th	1'11241	0'96524	0'95342	—	0'789	0'8262	0'76259	0'7521	0'79108	—	—	0'76259
92 U	1'06477	0'92014	0'90833	0'8029	0'7454	0'7866	0'71807	0'7084	0'75268	—	0'736	0'72413

Elements.	$\gamma_3$ .	$\gamma_1$ .	$\gamma_6$ .	$\gamma_2$ .	$\gamma_5$ .	$\gamma_4$ .
76 Os	—	1'02247	—	—	—	—
77 Ir	—	0'98841	0'9636	0'9636	0'9566	—
78 Pt	0'9855	0'95545	0'9317	0'9317	0'9256	0'8950
79 Au	0'9542	0'92437	0'90125	0'90125	0'89568	0'8663
81 Tl	0'8942	0'86529	0'8417	0'8447	0'8379	0'8100
82 Pb	0'8639	0'83708	0'81370	0'8182	0'81370	0'7836
83 Bi	0'8378	0'81065	0'7874	0'7929	0'7874	0'761
90 Th	—	0'65103	0'6301	—	—	—
92 U	—	0'61283	0'5926	0'6044	0'5970	—

TABLE

WAVE-LENGTHS OF THE LINES OF THE L SERIES

Elements.	$L$ .	$\eta$ .	$a_2$ .	$a_1$ .	$\beta_4$ .	$\beta_1$ .	$\beta_3$ .	$\beta_6$ .	$\beta_2$ .	$\gamma_5$ .	$\gamma_1$ .
37 Rb	—	8'0290	—	7'3027	6'8028	7'0604	6'7699	6'9675	—	6'7386	—
38 Sr	7'821	7'505	—	6'8478	6'3855	6'6092	6'3499	6'5030	—	6'2788	—
39 Yt	—	—	—	6'4349	6'0019	6'1984	5'9678	—	—	—	—
40 Zr	6'898	6'5931	—	6'0559	5'6527	5'8228	5'6182	5'6935	5'5734	5'4810	5'3730
41 Nb	6'509	6'195	5'717	5'7113	5'3314	5'4796	5'2959	5'3461	5'2253	—	5'0241
42 Mo	—	5'835	5'400	5'3943	5'0358	5'1658	5'0002	—	4'9092	4'8190	4'7111
44 Ru	—	—	4'84367	4'83567	4'5126	4'61100	4'4764	4'4764	4'3619	4'2766	4'17282
45 Rh	5'2070	4'9112	4'59556	4'58778	4'2778	4'36400	4'2413	4'2301	4'1221	4'0352	3'9357
46 Pd	4'9396	4'6502	4'36660	4'35850	4'0623	4'13730	4'0257	4'0070	3'9007	3'8116	3'71636
47 Ag	4'6976	4'4101	4'15382	4'14564	3'8611	3'92664	3'82445	3'7994	3'69383	3'6073	3'51485
48 Cd	4'4713	4'1875	3'95636	3'94782	3'67425	3'73008	3'63642	3'6073	3'5064	3'4181	3'32800
49 In	4'2593	3'9761	3'77242	3'76367	3'4990	3'54783	3'4619	3'4280	3'3312	3'2418	3'15529
50 Sn	4'0633	3'7818	3'60108	3'59218	3'3363	3'37792	3'2989	3'2622	3'1679	3'0774	2'99493
51 Sb	3'8803	3'5996	3'44075	3'43177	3'1843	3'21836	3'14514	3'1078	3'0166	2'9256	2'84507
52 Te	3'7101	—	3'29100	3'28199	3'0400	3'06997	3'0013	2'9644	2'8761	2'7831	2'70647
55 Cs	—	2'9833	2'89560	2'88610	2'6605	2'67784	2'62293	2'5875	2'5064	2'4111	2'34252
56 Ba	3'1287	2'8571	2'77902	2'76964	2'5498	2'56224	2'5110	2'4772	2'3993	2'3023	2'23660
57 La	3'000	2'734	2'66893	2'65968	2'4438	2'45330	2'4053	2'3739	2'2980	2'2008	2'13720
58 Ce	—	2'6147	2'56511	2'55600	2'3442	2'35100	2'3059	2'2769	2'2041	2'1056	2'04433
59 Pr	2'7781	2'507	2'46703	2'45770	2'2501	2'25390	2'2124	2'1859	2'1148	2'0161	1'95681
60 Nd	2'6703	2'4042	2'37563	2'36531	2'1622	2'16221	2'1222	2'0993	2'0314	1'9313	1'87383
62 Sa	2'4770	2'214	2'20568	2'19501	1'9964	1'99357	1'9580	1'9422	1'8781	1'7751	1'72309
63 Eu	2'3903	—	2'12733	2'11633	1'9221	1'91631	1'8827	1'8705	1'8082	1'705	1'6543
64 Gd	2'3071	—	2'05262	2'04193	1'8493	1'84246	1'8109	1'8031	1'7419	1'6376	1'58863
65 Tb	2'2290	—	1'98231	1'97149	1'7814	1'77268	1'7425	1'7375	1'6790	1'5742	1'5266
66 Dy	2'1540	1'8922	1'91564	1'90460	1'7167	1'70658	1'6777	1'6777	1'6198	1'5152	1'4697
67 Ho	2'0821	1'8220	1'85206	1'84098	1'6553	1'64352	1'6160	1'6188	1'5637	1'459	1'4142
68 Er	2'0151	1'7548	1'79140	1'78040	1'5964	1'58344	1'5579	1'5636	1'5106	1'403	1'3623
69 Tm	1'9511	1'6923	1'7339	1'7228	1'5412	1'5268	1'5023	1'5115	1'4602	1'3523	1'3127
70 Yb	1'8900	1'6310	1'6789	1'6679	1'4882	1'4725	1'4494	1'4627	1'4128	1'3030	1'2648
71 Lu	1'8318	1'5738	1'62636	1'61551	1'4372	1'4207	1'3982	1'4143	1'256	1'2203	1'1765
72 Ct	1'7774	1'5197	1'57704	1'56607	1'3893	1'3711	1'3497	—	1'3235	1'2121	—
73 Ta	—	—	—	—	—	—	—	—	—	—	—
74 W	—	—	—	—	—	—	—	—	—	—	—

\* Coster, *Phil. Mag.*, 1922, 1, p. 1070;

XXVA

ACCORDING TO COSTER.\* (ANGSTRÖM UNITS)

$\gamma_2$ .	$\gamma_3$ .	$\gamma_4$ .	$\beta_7$ .	$\beta_6$ .	$\beta_{10}$ .	$\beta_{11}$ .	$\beta_{12}$ .	$\beta_{13}(?)$ .	$\beta_{14}$ .	$\gamma_1$ .	$\gamma_8$ .	$\gamma_{10}$ .
6'0282	—	—	—	—	—	—	—	—	—	—	—	—
5'6294	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—
4'9412	—	—	—	—	—	—	—	—	—	—	—	—
4'639	—	—	—	—	—	—	—	—	—	—	—	—
4'3613	—	—	—	—	—	—	—	—	—	—	—	—
3'8879	—	—	—	—	—	—	—	—	—	—	—	—
3'6770	—	—	—	—	—	—	—	—	—	—	—	—
3'4809	—	—	—	—	—	—	—	—	—	—	—	—
3'2997	—	—	—	—	—	—	—	—	—	—	—	—
3'1316	—	—	—	—	—	—	—	—	—	—	—	—
2'9736	2'9191	3'317	3'2598	3'2658	3'3049	3'2959	—	—	—	—	—	—
2'8273	2'7713	3'149	3'1081	3'1144	3'1426	3'1347	—	—	—	—	—	—
2'6889	2'6336	$\beta_{11}$	2'9658	2'9725	2'9934	2'9858	—	—	—	—	—	—
2'5649	2'5057	—	—	—	—	—	—	—	—	—	—	—
2'2322	2'2270	2'1691	2'480	2'473	$\beta_7$	2'483	—	—	—	—	—	2'2369
2'1340	2'1295	2'0715	2'3756	2'3712	—	2'3817	—	—	—	2'218	2'218	2'1402
2'0416	2'0366	1'9787	2'270	2'277	2'285	—	—	—	—	—	—	2'0481
1'9559	1'9509	1'8952	2'1763	2'1810	2'1916	—	—	—	—	2'2121	2'029	2'019
1'8750	1'8699	1'8153	2'0874	2'0958	2'1025	—	—	—	—	2'1220	1'9422	1'9322
1'7974	1'7925	1'7408	2'0043	2'0117	2'0193	—	—	—	—	2'0388	1'859	1'8022
1'6559	1'6517	1'6033	1'8523	1'8581	1'8657	—	—	—	—	1'8871	1'8851	1'8593
1'5939	1'5877	—	1'784	1'788	1'796	—	—	—	—	1'9092	1'7814	1'644
1'5310	1'5259	1'4818	1'7196	1'7281	1'7381	—	—	—	—	1'8355	1'7481	—
1'4738	1'4683	1'4239	1'6558	—	1'664	—	—	—	—	1'7655	1'6851	—
1'4203	1'4139	1'3714	1'5957	—	—	—	—	—	—	1'6992	1'6251	—
1'3677	1'3613	1'3197	—	—	—	—	—	—	—	1'6355	1'567	—
1'3184	1'3118	1'2732	1'4892	1'4823	( $\beta_7$ )	1'5014	—	—	—	1'5756	1'512	—
1'2712	1'2653	1'2264	—	—	—	—	—	—	—	—	—	—
1'2256	1'2198	1'1820	—	—	—	—	—	—	—	—	—	—
1'1832	1'1775	1'1411	1'3459	1'3330	1'3398	—	—	—	—	—	—	—
1'1413	1'1356	1'1001	1'3035	—	—	—	—	—	—	—	—	—
—	—	—	1'2600	1'2429	1'2506	—	—	—	—	—	—	—
—	—	—	1'2208	1'2021	1'2094	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—

1922, 2, p. 549; 1923, 2, p. 956.

elements should tend to resemble luminous spectra by becoming more complex and losing their atomic character.

This resemblance depends to some extent on the depths of the levels on which are situated the electrons whose displacement gives rise to the emission of the lines on Bohr's theory. If these levels are relatively superficial (e.g. if the work of extraction is less than 5000 volts) external influences such as pressure, temperature, chemical combination, ionisation of the outside rings, and so on, will have an appreciable effect and will tend to change the simplicity of the very high frequency spectra.

*Spectra of the isotopes of lead.*—Several authors, notably Duane and Shimizu [54], Siegbahn and Stenström [55], and C. D. Cooksey [56], have carefully compared the L absorption limits and some emission lines of ordinary lead and of specimens of radioactive lead. They have not been able to observe any measurable difference (with an accuracy of  $10^{-4}$  Ångström units).

**6. Moseley's law of emission lines.**—Although Moseley discovered this law when examining lines of the K series, the equation which connects the square roots of the frequencies with the atomic numbers has only a simple significance for the frequencies of the absorption limits, and is only admissible to a first approximation for lines. The principle of combination, which seems now well established, shows that the frequencies of the lines, being equal to the differences between the frequencies of two levels, cannot, in fact, obey a law of the same type as Moseley's law. If the values of  $\sqrt{\nu}$  and  $N$  are plotted on a graph, lines of various curvatures are obtained, which can be interpreted by reference to the curves for the absorption limits.

The "double-entry" table, Table XXVI, shows what are now considered to be the most probable assignments of the lines, and the levels which correspond to them according to the principle of combination.

**7. Experimental basis of the principle of combination.—**

Kossel [38] (see also Barkla [39]) was the first to draw attention to the relations between the absorption discontinuities and the emission lines of a substance which follow from Bohr's theory, and the existence of which was confirmed by the first measurements of X-ray spectra.

As research progressed, some "defects of combination" seemed to arise and theoretical explanations of these have been attempted, but errors in nomenclature of the lines have also occurred (see Dauvillier, Coster, etc.) and Kossel's relations now appear to be well established.

The best experimental basis on which the principle of combination rests is found in the accurate measurements of Duane and Shimizu [40], Duane and Stenström [40], Coster [40], and Dauvillier [40]. Duane and Stenström have published the following table in which  $K\alpha$ ,  $L\alpha$ , . . . are the wave numbers  $\left(\frac{1}{\lambda}\right)$  of the absorption discontinuities, and  $K\alpha$ ,  $L\beta$ , . . . are the wave numbers of the lines of the K and L series of tungsten.

$$\begin{array}{l} K\alpha - L\alpha_1 = 4.792 \pm 0.003 : K\alpha_1 = 4.7938 \pm 0.001 \\ K\alpha - L\alpha_2 = 4.685 \pm 0.003 : K\alpha_2 = 4.6858 \pm 0.0007 \\ K\alpha - L\alpha_3 = 4.639 \pm 0.006 : K\alpha_3 = 4.65 \pm 0.02 \\ K\alpha - M\alpha_3 = 5.433 \quad : K\beta = 5.429 \end{array}$$

**8. The principle of selection.**—Spectral lines are obtained by the "combination" of two critical frequencies but the converse does not always hold; every "combination" of two critical frequencies does not necessarily give the frequency of a line which is actually present; experiment is far from showing all the predicted lines. It must be possible to find, therefore, a "principle of selection" which will indicate whether a particular line predicted by the principle of combination really exists.

Two theoretical attempts have been made to determine this principle of selection. Rubinovicz is responsible for the following idea: "When one of Bohr's electrons jump

from one stable trajectory to another the moment of its momentum changes by a whole multiple of  $\frac{h}{2\pi}$ . If the atom considered is not subject to any exterior force such as an electric or a magnetic field, the moment of the momentum of the system (atom in the final state + radiation emitted) must be equal to that of the atom in the initial state." By developing this idea and by making certain assumptions, inspired by the electromagnetic theory, on the symmetry of the radiation emitted, Rubinovicz arrived at the following principle. "Only those lines are actually emitted which correspond to a variation by unity (plus or minus) of one of the quantum numbers (the azimuthal quantum number) which characterise the trajectory."

Bohr arrived at a similar statement by employing his principle of correspondence, developing the movement of the electron in its initial and final trajectories in a Fourier series, and saying that the harmonics missing in these two movements must also be missing in the emitted radiation.

The application of the Rubinovicz-Bohr principle of selection is simple in the case of Sommerfeld's plane atom. On the other hand, it is very difficult if Smekal's ideas are adopted, as they must be nowadays. Wentzel has stated an empirical rule, and it is easy to find others by using the results of Bohr and Rubinovicz. None of them, however, seems to be rigorous, and none of them is capable of accounting for all the details of the experimental results.

### **9. The excitation of secondary rays by primary X-rays.—**

Sagnac was the first to show that matter exposed to X-rays itself emits radiation, part of which at least is different from the primary radiation. Barkla examined this re-emission in a series of fundamental researches; the secondary radiation consists of two parts, one identical with the incident rays and produced by scattering, the other resulting from a transformation of the incident radiation by the atoms which act as convertors. It has been mentioned elsewhere (Chap. I), that the fluorescent radiations thus emitted are

themselves divided into two classes, periodic rays (fluorescent X-rays) and corpuscular rays (secondary  $\beta$ -rays) ; these latter will be studied in Chapter VI.

Before it was known that X-rays could be diffracted, the different kinds were distinguished by their physical properties, and above all by their absorption coefficients. In this way Kaye had been able to show that the fluorescent X-rays which are emitted by a substance exposed to primary X-rays are identical with the radiations which the same substance yields when it is used as the anticathode of an X-ray tube. Barkla had extended Stokes' law to the fluorescence of X-rays ; we can now go further and say that a beam of X-rays of frequency  $\nu$  will excite a series of lines of an element, for example, the K series, provided that  $\nu$  is greater than the frequency  $\nu_K$  of the K absorption discontinuity of the substance which serves as the secondary radiator.

*Thus, the laws of the excitation of a series of lines of a substance, both when the substance acts as the anticathode under the bombardment of the cathode electrons, and when it radiates by fluorescence through exposure to X-rays, can be combined in the same statement, by saying that in all cases the lines of the series appear when the quantum of the exciting radiation (corpuscular or undulatory) is equal to or exceeds the quantum of the corresponding absorption discontinuity.\**

This is true for the excitation of the characteristic rays of a body exposed to X-rays.

X-ray spectra can be studied by taking as a source, not an anticathode, but a secondary radiator exposed to a primary beam. The intensity will be less but this inconvenience is often compensated by the great convenience which results from this arrangement because the substances to be examined do not have to be introduced into a vacuum and placed at the focus of a cathodic bombardment. M. de Broglie [41] showed in this way that the law  $\sqrt{\nu} = AN + B$

\* This law can be considered to be proved in particular by the results given in Chapter VI, which concern the emission of secondary electrons by the action of X-rays.



is valid for a number of substances which Moseley could not examine. Among these substances were iodine and tellurium, the order of which in the periodic table had had to be inverted. The X-ray spectrum has justified this classification by showing that the atomic numbers of these two elements are in inverse order to their atomic weights.\*

Fine and intense lines can be obtained by this method with suitable apparatus, and it has the great advantage that it permits the investigation of the influence which external physical conditions or agents, such as temperature, magnetic field, etc., may exert on the emission.

To a first approximation the lines emitted as secondary radiation [41] have the same wave-lengths as the lines excited in tubes. Perhaps on closer investigation it might be found that the influences just mentioned introduce appreciable modifications in the intensity or position of the lines.

Dauvillier has shown, in particular for the K spectrum of iron, that appreciable differences exist between the intensities of the lines emitted directly by an anticathode and those given by the fluorescence of a secondary radiator. The spark lines which characterise a very strongly ionised atom tend to disappear in the spectrum of the secondary rays where the atom is not subjected to the cathodic bombardment [74].

The elements of medium and high atomic weight readily emit their line spectra when exposed to suitable X-rays; Barkla discovered some time ago that in the case of the light elements the secondary radiation consists principally of scattered primary rays.

A. H. Compton [52] has repeated Barkla's old experiments and has obtained results which appear to indicate interesting phenomena. He exposed a secondary radiator of celluloid or aluminium to an approximately monochromatic radiation (K rays of molybdenum) and examined

\* An analogous inversion exists for nickel and cobalt and is similarly justified by X-ray spectra (Moseley).

the secondary spectrum emitted in a direction nearly normal to that of the primary rays.

At first the spectrum obtained showed the molybdenum lines (re-emitted by scattering), but subsequently there was an appreciable continuous spectrum, the spectrum of the incident rays being scarcely distinguishable. This continuous spectrum exhibited a well-marked maximum at about  $0.95 \text{ \AA.}$ , which is about one-third greater than the wave-length of the incident rays.

Compton has also commenced researches on the state of polarisation of the secondary radiation.

It has been mentioned that the energy absorbed when secondary radiations are produced is divided between secondary X-rays and secondary rays; how does the division occur? It is probable, as Barkla [42] has deduced indirectly, that everything depends on the difference  $\nu - \nu_K$ , between the frequencies of the exciting radiation and the absorption discontinuity concerned. When  $\nu - \nu_K$  is small the ratio of the energy of the secondary  $\beta$ -rays to that of the secondary X-rays is nearly unity; as  $\nu - \nu_K$  increases, the ratio becomes greater and greater. An attempt has been made to explain this result theoretically [61].

**10. The emission of X-rays of very long wave-length and the continuity between these rays and the extreme ultra-violet.**—The investigations of Schumann and Lyman made the examination of the ultra-violet spectrum possible down to about  $500 \text{ \AA.}$ ; Millikan [37], by using intense high tension sparks in a vacuum, has succeeded in obtaining, and in measuring with a grating, lines of wave-length as low as  $144 \text{ \AA.}$  He has measured strong lines of aluminium, magnesium, and sodium with wave-lengths of  $143.3 \text{ \AA.}$ ,  $232.2 \text{ \AA.}$ ,  $372.2 \text{ \AA.}$ , which seem to be the La lines of these elements. These lines fall into position on the prolongation of the Moseley curve for heavier elements, and indicate that the regularity of the L series holds as far as atomic number 10.

Between  $143.3 \text{ \AA.}$  and  $1200 \text{ \AA.}$  there is no emission line of aluminium. This would correspond to the interval which

separates the L series from the M series, and analogous results are found for magnesium and sodium. Millikan has completed this investigation by an extensive research on the region which extends from 150 Å. upwards and includes the beginning of the ultra-violet, but an account of this is outside the scope of this book.

On the other hand, on account of the limitations imposed by the values of the crystalline reticular distances, which in practice do not exceed  $10^{-7}$  cm., the study of X-ray spectra by means of crystals has not been possible for radiations of wave-length greater than about 12 Å. Thus a region exists between 12 and 144 Å. the investigation of which requires special methods.

Up to the present the evaluation of wave-lengths in this new region has been carried out by the extrapolation of the results by which the emission of X-rays, produced by the bombardment of an anticathode by cathode rays, has been connected with the quantum of the bombarding electrons. The arrangement generally employed is as follows: in a highly evacuated enclosure electrons from an incandescent cathode fall through a known potential difference on an anticathode. The radiations which the latter emits are detected either by the ionisation which they produce in a chamber containing a gas (and then, of course, it is necessary to separate the gas from the vacuum by a very thin partition), or by the photoelectric effect excited on a metal plate connected to a sensitive electrometer. In the latter case, a series of conductors at suitable potentials forming an electrostatic trap must be placed along the path of the rays from the anticathode in order to prevent spurious charges from reaching the plate.

The radiation may also be observed, as was shown long ago by Sir J. J. Thomson [43], by its action on a photographic emulsion of the Schumann type.

It is usually found that when the quantum of the cathode electrons is increased the photoelectric effect by which the rays are detected increases suddenly at a definite point.

Analogy with high frequency X-rays leads to the belief that a new series of rays characteristic of the anticathode are then excited, i.e. the quantum of the cathode rays at this instant just exceeds the quantum of a discontinuity of the element of which the anticathode is made. (Dember [44], Richardson and Bazzoni [45], Dadourian [46], Hughes [47], Kurth [48].)

Tables XXVII and XXVIII give some wave-lengths thus obtained.

TABLE XXVII \*

Elements.	K Series.	L Series.	M Series.	N Series.
Carbon . . .	42.6 Å.	375 Å.	—	—
Oxygen . . .	23.8	248	—	—
Aluminium . . .	—	100	326 Å.	—
Silicon . . .	—	82.5	—	—
Titanium . . .	—	24.5	85.3	—
Iron . . .	—	16.3	54.3	247 Å.
Copper . . .	—	12.3	41.6	116

TABLE XXVIII

Elements.	Richardson.	Hughes.	Holweck.
Carbon K . . .	43 Å.	57.5 Å.	43 Å.
Carbon L . . .	—	358	—
Aluminium L . . .	—	—	193.5
Molybdenum M . . .	34.8	—	—
Boron K . . .	—	83.5	77
Boron L . . .	—	505	—

From what has just been said, these numbers are especially characteristic of the absorption discontinuities ; their exact significance is a matter for discussion, but they certainly indicate emission regions for the elements concerned.

Mohler and Foote (*Scientific Papers of the Bureau of Standards*, No. 425, December, 1921, and *Phys. Rev.*, 1922, 1, p. 434) have described a slightly different method of investigating the X-rays of long wave-length which can be emitted by gases and vapours. A discharge in a gas is produced by

\* Kurth, *Phys. Rev.*, December, 1921, 18, p. 461.

means of a hot cathode, and the photoelectric effect, on an electrode suitably screened, of the radiations coming from this type of arc discharge is examined.

The photoelectric current is approximately a linear function of the discharge voltage, but exhibits sharp elbows at certain values of this potential difference. The results of measurements of these elbows are given in Table XXIX ; it will be observed that it contains two or three values for the L discontinuities. The authors tried to compare these experimental results with the indications afforded by the X-ray spectra of the same elements. The principal limit appears to be in good agreement with the  $L_1$  and  $L_2$  discontinuities of the ordinary nomenclature, but the others correspond, by Kossel's relation,

$$L_p \text{ discontinuity} = K \text{ discontinuity} - K_p \text{ line,}$$

to lines in the K spectrum other than  $\alpha_1$  and  $\alpha_2$ . This should form a further proof of the more complex structure which is assumed by the levels of the light elements.

TABLE XXIX \*

Elements.	N.	Volts.	K Discontinuity $\lambda$ in $\text{\AA}$ .	L Discontinuity $\lambda$ in $\text{\AA}$ .
Boron . . .	5	186	66.4	—
	—	125	—	—
Carbon . . .	6	272	45.4	—
	—	234	—	—
Nitrogen . . .	7	374	33.0	—
	—	352	—	—
Oxygen . . .	8	478	25.8	—
Sodium . . .	11	35	—	353
	—	17	—	725
Magnesium . . .	12	46	—	268
	—	33	—	374
Phosphorus . . .	15	126	—	98
	—	110	—	112
	—	95	—	130
Sulphur . . .	16	152	—	81.2
	—	122	—	101
Chlorine . . .	17	198	—	62.3
	—	175	—	70.5
	—	157	—	78.6

\* Mohler and Foote, *Phys. Rev.*, 1922, 1, p. 434.

Holweck [49] carried out his investigations by the ionisation method, the radiation being passed through a very thin celluloid film, and he found that his results could be explained if it were assumed that when the anticathode is subject to the impact of cathode rays of quantum  $h\nu$ , it emitted a continuous spectrum bounded on the high frequency side by the frequency  $\nu$ . After filtration only approximately homogeneous rays remained, and these were

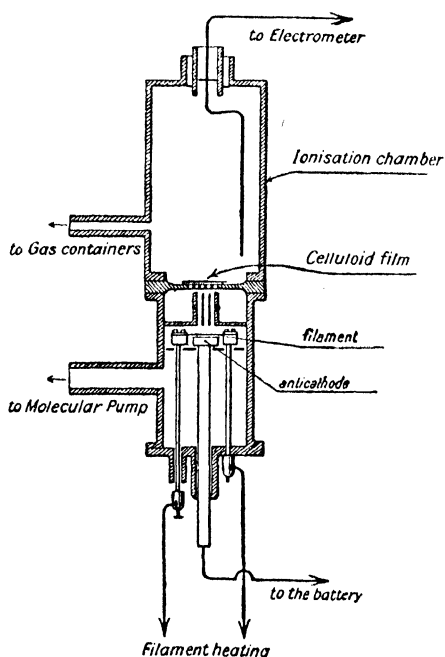


FIG. 17.

in the most penetrating region and had a frequency nearly equal to the maximum  $\nu$ . Here the influence of the characteristic rays excited at the anticathode is negligible. In this way Holweck arrived at some remarkable results, especially for absorption.

A brief description of the apparatus (Fig. 17) which he used in his experiments will now be given. A first metallic chamber (in the lower part of the figure) is in communication

with a molecular pump, and contains a filament and an anticathode between which a known difference of potential is maintained; the metallic walls are double and water circulates in the space between them. A number of parallel tubes placed above the filament cut off the oblique rays; sometimes a supplementary screen is also interposed when low potentials are being used, in order to prevent any photo-electric action from being exerted by the light from the incandescent cathode. A very thin sheet of celluloid (0.7 to 0.8 .  $10^{-5}$  cm. thick), obtained by the evaporation of an alcoholic solution, is reinforced by a grille and separates the lower part from the ionisation chamber. Such sheets are impermeable to the cathode rays employed and can support a difference of pressure of several cm. of mercury.

The absorption of the rays produced can be examined either in terms of the length and density of the layer of gas traversed or in terms of the thickness of the celluloid diaphragm.

In this way Holweck has found a large number of radiations extending from 10 to 493 Å., and has been able to show that the rays emitted follow, at least as far as 100 Å., the same absorption law as true X-rays, in the gases used (nitrogen and oxygen).

It has been possible to measure the absorption by celluloid right up to the ultra-violet; the curve showing the relation between the absorption coefficient and the wavelength exhibits a maximum at about 80 Å. and decreases on either side.

In short, radiations of various wave-lengths have been examined by these different authors in a region which completely connects the ultra-violet and X-rays. Holweck's work, especially, seems conclusively to establish the continuity.

The method of secondary  $\beta$ -rays (Chap. VI), by means of which X-ray spectra can be obtained without using crystals, will very probably be capable of successful application in this region.

G. Reboul [57] has shown that if a substance which is a bad conductor of electricity be traversed by a current under suitable conditions it produces an effect on a photographic plate. He has attributed this effect to the existence of a very absorbable radiation which should be situated between the ultra-violet and the X-rays. The interpretation of this phenomenon and the spectral region of the radiation emitted are still rather uncertain.

**11. Analysis by X-ray spectra.**—The simplicity of high-frequency spectra, the regularity of their structure, and Moseley's law, make X-rays very suitable for ascertaining the presence of elements by means of their characteristic radiations. Accurate data concerning the sensitiveness of this method of analysis are not yet available, but the existence of impurities in an anticathode, even in very small quantities, causes the appearance of foreign lines in the spectrum. The method of secondary rays, though less sensitive, can be used advantageously with suitable apparatus and exposures.

There are five empty spaces in Mendéléeff's table; numbers 43, 75, and 85 in the seventh group, number 87 in the first group, and number 81 which is between neodymium and samarium. X-ray spectra have already settled the order of the rare earths by demonstrating without ambiguity which substances are elements, and especially so by confirming the separation by Urbain of the old ytterbium into neoytterbium, 70, and lutecium, 71, and by verifying the elementary nature of thulium, 69. The existence of celtium, the third constituent of ytterbium found by G. Urbain, could not be established, at first, on account of the very low celtium content of existing preparations. Dauvillier [53], by carefully examining the spectrum of one of these preparations, has found two very feeble lines  $\alpha_1 = 1.5618 \text{ \AA.}$  and  $\beta_2 = 1.3194 \text{ \AA.}$ , close to numerous ytterbium and lutecium lines. These would appear to belong to the L series of the element 72 and should thus confirm the existence of celtium.



By means of noteworthy researches, the results of which were published for the first time in *Nature* (January, 1923), Coster and von Hevesy have been able to show that the minerals containing zirconium also contain a very appreciable proportion of a new element, the X-ray spectrum of which marks it as possessing the atomic number 72. Theoretical conceptions due to Bohr indicated to them that the element 72 should be a homologue of zirconium. It is certain that the new element, abundant in zirconia, is identical with the celtium of Urbain and Dauvillier; the Danish authors have given it the name of hafnium and this question of nomenclature is not yet settled.

So far, no other new element has been discovered by means of X-rays, but it seems as though success must be obtained very soon, since the chemical group to which the unknown elements belong and the region of the spectrum in which their lines must be sought are known by means of the periodic table and Moseley's law respectively.

The high-frequency emission and absorption spectra of radium only among the radioactive elements have been examined.

## **12. The reflection and the diffraction by a slit of very soft X-rays: total reflection.**

*Diffraction.*—By using a linear source of soft X-rays, consisting of an anode of tungsten wire  $12\mu$  in diameter, bombarded by low velocity electrons, and a slit of width about  $6\mu$ , Holweck [68] has been able to show that rays corresponding to 1620 volts are still not appreciably diffracted, but that with rays of 260 volts (about  $50 \text{ \AA}$ .) a very appreciable broadening of the image of the slit indicates the commencement of the phenomena of optical diffraction. (See Plate 3.)

*Reflection.*—With a similar arrangement the same author has been able to establish an appreciable reflection at a well-polished bronze mirror of a beam of rays ( $\lambda$  from 100 to  $300 \text{ \AA}$ .) incident at an angle of about  $12^\circ$  with the plane of the mirror.

# DIFFRACTION OF SOFT X-RAYS

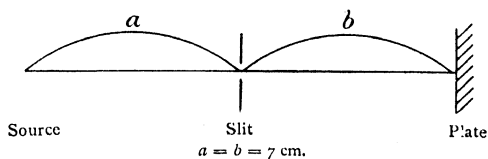
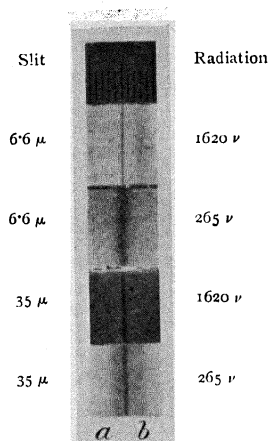


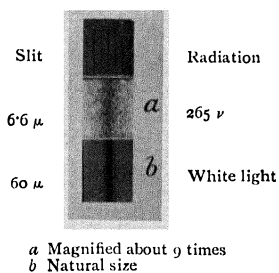
FIG. 1



The band *a b* is due to a screen on which stray electrons were incident

FIG. 2

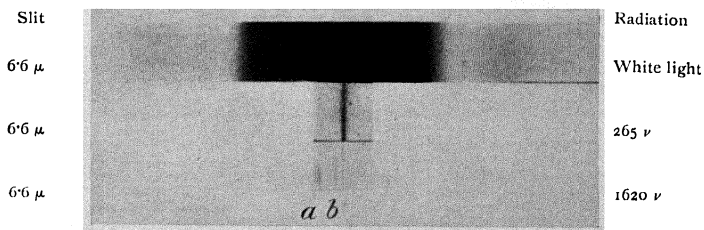
(One small division of the micrometer scale = 0.01 cm.)



*a* Magnified about 9 times  
*b* Natural size

FIG. 3

Magnified about 3 times



*a* and *b* are due to corpuscular rays deviated by an electric field

FIG. 4



Gouy [69] has pointed out that such experiments foreshadow the possibility of constructing, for soft X-rays, reflecting microscopes capable of resolving details at least fifty times finer than those shown by ordinary microscopes.

*Total reflection.\**—Compton [70] has endeavoured to explain the small discrepancies between Bragg's law and the observed facts by assuming the existence of a refractive index very near to unity; this would lead to the prediction of total reflection at an angle of about 12 minutes. Compton has experimented with various wave-lengths and with mirrors of glass and silver and has concluded from his results that total reflection really exists at very small angles.

These facts should be connected with the results published by Wolfers [71], relative to a fringe which, under certain conditions, may limit the apparent contour of shadows cast by X-rays.

**13. Analogy between optical spectra and X-ray spectra** [72].—In a large number of cases it has been possible to group the optical spectral lines of an element in series. The frequencies of the lines of a series are the differences between a constant term, which is the same for all the lines of the series, and a term varying from one line to another. This fact is easily interpreted on Bohr's theory by saying that all the lines of a series are produced by the passage of an electron from various departure levels to the same level of arrival. In the case of hydrogen the terms are of the form  $\frac{R}{n^2}$  where  $R$  is Rydberg's constant and  $n$  a whole number. It will be recalled that the formula of Balmer's series is

$$\nu = \frac{R}{2^2} - \frac{R}{m^2}, \quad (m \geq 3).$$

For many other elements (notably the alkalis and the alkaline earths) it has been possible to establish optical series obeying a regular law, but the series term is more complicated than in the case of hydrogen; its investi-

\* See also Appendix I, p. 191.

gation is principally due to Rydberg and Ritz. We shall designate it briefly  $\frac{R}{(n+a)^2}$ ;  $R$  is Rydberg's constant,  $n$  the total number of quanta of the corresponding level, and  $a$  a function of the distribution of this number between the degrees of freedom. Usually  $\frac{R}{(n+a)^2}$  is represented by the symbol  $(n, a)$ .

Optical spectroscopy has shown that the function  $a$  can assume a series of values designated by  $s, p, d, b, \dots$  so that the optical terms can be collected in the following table :—

(1, s)	(2, s)	(3, s)	(4, s)	(5, s)
	(2, p)	(3, p)	(4, p)	(5, p)
		(3, d)	(4, d)	(5, d)
			(4, b)	(5, b)

The series formulæ are combinations of these terms. The best-known are :—

Principal series	. (1, s) — (m, p)	$m = 2, 3 \dots$
Diffuse series	. (2, p) — (m, p)	$m = 3, 4 \dots$
Sharp series	. (2, p) — (m, d)	$m = 3, 4 \dots$
Bergmann's series	. (3, d) — (m, p)	$m = 4, 5 \dots$

The  $K, L, \dots$  levels in the X-ray region are also characterised by a total number of quanta  $n$  and their distribution between the various degrees of freedom. It is therefore natural to expect to find again in X-ray spectra a classification of the terms and consequently a distribution of the lines analogous to that of optics. This is indeed the case. The terms  $K, L_3, M_6, \dots$  take the place of the terms  $s$ ; the terms  $L_1, L_2, M_5, M_4, \dots$  that of the terms  $p$ ; the terms  $M_3, M_2, M_1, \dots$  are the terms  $d$ ; and so on.

The  $K$  series is a principal series; the  $L_3$  series a second principal series [(2, s) — (m, p)].

The  $L_1$  and  $L_2$  series resolve themselves into a diffuse series and a sharp series. The general tendencies and the

fine structure of these X-rays series are in good agreement with those of optical series. There is a profound analogy and it has been a valuable guide in the most recent classifications.

## BIBLIOGRAPHY

1. M. DE BROGLIE, *Les progrès de nos connaissances concernant les rayons de Röntgen*. Conférence à la Société de Physique, Dec., 1913, *Les progrès de la Physique moléculaire*, p. 47.
2. D. L. WEBSTER, *Phys. Rev.*, 1917, 1, p. 220.
3. D. L. WEBSTER, *A problem concerning the emission of X-rays*. BERGEN DAVIS, *The intensity of emission of X-rays*. *Bulletin of the National Research Council*, No. 7, Dec., 1920.
4. DUANE and HUNT, *Phys. Rev.*, 1915, 2, p. 166.
5. RUTHERFORD, *Phil. Mag.*, 1915, 2, p. 339.
6. HULL, *Phys. Rev.*, 1916, 1, p. 156.
7. LEDOUX-LEBARD and DAUVILLIER, *Comptes Rendus*, 1916.
8. BLAKE and DUANE, *Phys. Rev.*, 1916, 2, p. 624.
9. WAGNER, *Ann. der Phys.*, 1918, 57, p. 403.
10. BIRGE, *Phys. Rev.*, 1919, 2, p. 361.
11. BERGEN DAVIS, *Phys. Rev.*, 1917, 1, p. 64, and 1918, 1, p. 433.
12. L. BRILLOUIN, *Comptes Rendus*, 1920, 1, p. 274.
13. D. L. WEBSTER, *Phys. Rev.*, 1917, 1, p. 220, and *Nat. Acad. Sci. Proc.*, 5 May, 1919, p. 163.
14. LEDOUX and DAUVILLIER, *La Physique des rayons X*.
15. KAYE, *Phil. Trans.*, 1908.
16. BRAININ, *Phys. Rev.*, 1918, 1, p. 461.
17. DUANE and SHIMIZU, *Phys. Rev.*, 1918, 1, p. 491.
18. ULREY, *Phys. Rev.*, 1918, 1, p. 401.
19. DORN, *Ann. der Phys.*, 1897, 63, p. 160.  
WIEN, *Ann. der Phys.*, 1905, 5, p. 991.  
E. CARTER, *Ann. der Phys.*, 1906, 21.  
ANGERER, *Ann. der Phys.*, 1906, 21.  
RUTHERFORD and MACCLUNG, *Proc. Roy. Soc.*, 1900.  
BEATTY, *Proc. Roy. Soc.*, 1913-1914.  
RUTHERFORD and BARNES, *Phil. Mag.*, 1915, 1, p. 361.
20. WEEKS, *Phys. Rev.*, 1917, 2, p. 564.
21. RÖNTGEN, *Berliner Ber.*, 1897.
22. WALTER, *Fortschr. a. d. Geb. d. Röntgenstr.*, 11, 1907.
23. BASSLER, *Ann. der Phys.*, 28, 1909, p. 808.
24. BARKLA, *Phil. Trans.*, 1905, p. 467.

25. HAGA, HERWEG, and VEGARD, *Ann. der Phys.*, July, 1907, p. 439; *Ann. der Phys.*, May, 1909, p. 398; *Proc. Roy. Soc.*, 1910.
26. KAYE, *Proc. Camb. Phil. Soc.*, 1909, p. 269.
27. STARK, *Phys. Zeits.*, 1909, p. 902.
28. LOEBE, HAM, MILLER, FRIEDRICH, and KIRSCHBAUM, *Ann. der Phys.*, 1914, 44, p. 1033; *Phys. Rev.*, 1910, 1, p. 96; *Jour. Franklin Inst.*, 171, May, 1911, p. 457; *Ann. der Phys.*, 1912, 2, p. 377; *Ann. der Phys.*, 1915, 1, p. 85.
29. WAGNER, *Phys. Zeits.*, 1920, p. 621. *Report on the continuous spectrum of X-rays. Jahrbuch der Radioaktivität und Elektronik*, 16 Dec., 1919, p. 212.
30. WHIDDINGTON, *Proc. Roy. Soc.*, July, 1911.  
BEATTY, *Proc. Roy. Soc.*, Dec., 1912.
31. D. L. WEBSTER, *Phys. Rev.*, 1916, 1, p. 599.
32. D. L. WEBSTER and CLARK, *Nat. Acad. Proc.*, 1917, p. 181.
33. A. DAUVILLIER, *Journal de Physique*, 1922.
34. WOOTEN, *Phys. Rev.*, 1919, p. 71.
35. M. DE BROGLIE, *Comptes Rendus*, 1920, 170, pp. 1053 and 1245.
36. DUANE and STENSTRÖM, *Phys. Rev.*, 1920, 1, p. 329; *Nat. Acad. Proc.*, 1920.
37. MILLIKAN, *Nat. Acad. Proc.*, 1920; *Phys. Rev.*, 1920; *Astrophys. Jour.*, July, 1920, 52; *Nat. Acad. Proc.*, Oct., 1921, p. 289.
38. KOSSEL, *Soc. All. de Phys.*, 1914.
39. BARKLA, *Nature*, 1915.
40. DUANE and SHIMIZU, *Phys. Rev.*, 1919, 2, p. 67.  
DUANE and STENSTRÖM, *Nat. Acad. Proc.*, Aug., 1920.  
COSTER, *Comptes Rendus*, 1921, 1, p. 1177.  
DAUVILLIER, *Comptes Rendus*, 1921 and 1922.
41. M. DE BROGLIE, *Comptes Rendus*, 1914, 1, pp. 1493 and 1785; *Comptes Rendus*, 1914, 2, p. 304; *Jour. de Phys.*, July, 1916, p. 3.
42. BARKLA, *Bakerian lecture*, 1917.
43. SIR JOSEPH THOMSON, *Phil. Mag.*, 1914, 2, p. 620.
44. DEMBERG, *Phys. Zeits.*, 1913, p. 1157.
45. RICHARDSON and BAZZONI, *Phil. Mag.*, 1917, p. 285, and 1921, 2, p. 1015.
46. DADOURIAN, *Phys. Rev.*, 1919, p. 234.
47. HUGHES, *Phil. Mag.*, 1922, 1, p. 145.
48. KURTH, *Phys. Rev.*, 1921, 2, p. 461.
49. HOLWECK, *Thèse de Doctorat; Comptes Rendus*, 1920, 2, p. 849, and 1921, 1, p. 439.
50. ELIZABETH R. LAIRD and VOLA P. BARTON, *Phys. Rev.*, 1920, 1, p. 297.

51. V. DOLEJSEK, *Nature*, 6 May, 1922.
52. A. H. COMPTON, *Phys. Rev.*, 1922, 1, p. 267.
53. A. DAUVILLIER, *Comptes Rendus*, 1922, 1, 1319.
54. DUANE and SHIMIZU, *Nat. Acad. Proc.*, 1919, p. 198.
55. SIEGBAHN and STENSTRÖM, *Phys. Zeits.*, 1917, 18, p. 547.
56. C. D. and D. COOKSEY, *Phys. Rev.*, 1920, 2, p. 329.
57. G. REBOUL, *Comptes Rendus*, 1921, and 1922, 2, p. 1452.
58. D. L. WEBSTER, *Nat. Acad. Proc.*, Nov., 1919, p. 26.
59. WAGNER, *Phys. Zeits.*, 1920, p. 621.
60. R. LADENBURG, *Methods of measuring the elementary quantum of action*, Hirzel, Leipzig, 1921.
61. M. and L. DE BROGLIE, *Comptes Rendus*, 1921, 2, p. 527.
62. A. H. KRAMERS, *Phil. Mag.*, 1923, 46, p. 836.
63. H. KUHLENKAMPFF, *Ann. der Phys.*, 1923, 69, 548.
64. WAGNER and KUHLENKAMPFF, *Phys. Zeits.*, 1922, p. 503.
65. KIRKPATRICK, *Phys. Rev.*, July, 1923, p. 37.
66. WEBSTER, *Phys. Rev.*, March, 1923, p. 312.
67. KIRKPATRICK, *Phys. Rev.*, Sept., 1923, p. 226.
68. HOLWECK, *Comptes Rendus*, 1923, 176, p. 570.
69. GOUY, *Comptes Rendus*, 1923, 176, p. 807.
70. COMPTON, *Phil. Mag.*, June, 1923, p. 1121.
71. WOLFERS, *Comptes Rendus*, 1923, 20, 1, p. 1385.
72. L. DE BROGLIE and A. DAUVILLIER, *Comptes Rendus*, 1922, 175, pp. 685, 785, 1198. *Journal de Physique*, 1924.
73. A. DAUVILLIER, *Ann. der Phys.*, March, 1920, IX, 13, pp. 49-134.
74. A. DAUVILLIER, *Comptes Rendus*, 1923, 3, 2, 177, p. 167.

See also the extensive bibliography published by M. Siegbahn: *Bericht über die letzte Entwicklung der Röntgenspektroskopie. Jahrbuch der Radioaktivität und Elektronik*, 1922, band 18, heft, 3, as well as several notes by Coster, Smekal, Wentzel, Hjalmar, etc., concerning the details of the structure of spectra, and published in the *Zeits. für Physik* of 1921.



## CHAPTER V

### SPECTROGRAPHS AND SPECTROMETERS

**1. General indications.**—All X-ray spectroscopy is based on the fundamental formula

$$n\lambda = 2d \sin \alpha.$$

This states, in fact, that a complex beam of rays incident on a face of a crystal is dispersed, for different values of  $\alpha$ , in a number of beams each of which is monochromatic if only the first order is considered. The superposition of different orders may occur as with grating spectra of luminous rays. Fortunately they are not, in general, very confusing.

A geometrical property, also first announced by Bragg, should be added to the preceding formula. This property is important because it serves the same purpose as the lenses of an optical spectroscope, by allowing the rays to be concentrated to a focus, so that, to some extent monochromatic images of the slit which serves as a source are obtained. These images of a rectilinear slit are the lines of the new spectrum. Let a pencil of rays of known angle emerge from S (Fig. 18), a source of monochromatic rays characterised by an angle of selective reflection  $\alpha$  at the face AB of a crystal which can be rotated about an axis O. Suppose that when the crystal is in the position AB the angle AOS is exactly equal to  $\alpha$ ; the central ray will be reflected along OS', and if the crystal continues to turn in the direction of the arrow, the ray SC of the beam will strike the reflecting plane shortly afterwards at the angle  $\alpha$  and will be reflected along CS'.

It can be shown geometrically that all the reflected rays such as CS' will cut the ray OS' at the same point S', such that OS' is equal to OS. In other words, the image of a

slit with respect to a rotating crystal, the axis of rotation being parallel to the slit, will be obtained by the following arrangement (a right section of the system being considered).

Let  $S$  be the position of the slit which is used as a source, and  $O$  the axis of rotation of the crystal; join  $SO$  and draw  $OS'$  such that the angle  $SOS'$  is equal to  $180 - 2\alpha$  (corresponding to the wave-length employed). Cut off  $OS'$  equal to  $OS$  and the image of  $S$  is at  $S'$ . Moreover, the size of the image  $S'$  is equal to that of the slit  $S$ , whatever the value of  $SO$ . The locus of  $S'$ , i.e. the focal surface, is cylindrical.

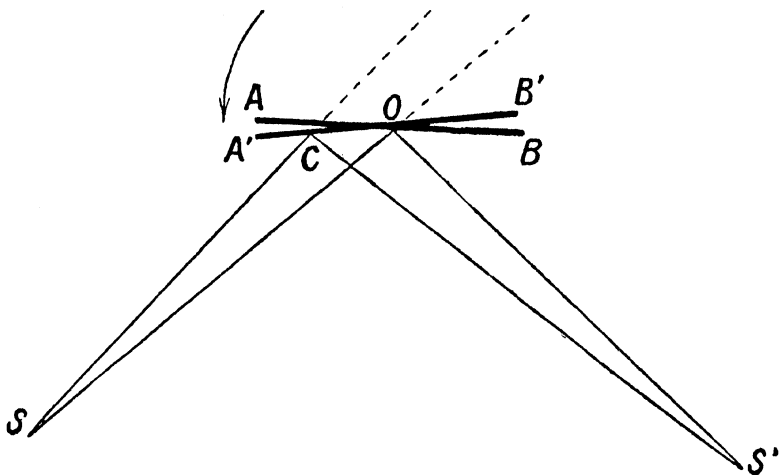


FIG. 18.

First Bragg [1] and then Moseley and Darwin [2] examined the reflected beams by receiving them in an ionisation chamber carried on the arm of a goniometer. The crystal was moved through a small angle, then the ionisation chamber through twice the angle to receive the reflected ray, and the ionisation current was measured by an electroscope. When the intensities of the ionisation current were plotted against the angle of incidence on the crystal, curves were obtained like that shown in Fig. 2. Peaks will be observed in this curve; these correspond to brilliant lines standing out from a more or less well-marked background.

The images formed when the crystal is continuously rotated can be registered on a sensitive plate (de Broglie, 1913 [3]) if the rotation is slow and uniform, e.g. if it is accomplished by means of clockwork as in self-recording barometers (Fig. 1, Plate 4). This arrangement is very good for obtaining extended spectra of great purity; the examination of the continuous spectrum, and thus of the absorption phenomena which are exhibited by such spectra, can be carried out in this way; the spectra obtained are similar to optical spectrograms. The substitution of this method for the ionisation method has made possible the change from curves such as that shown in Fig. 19 to the

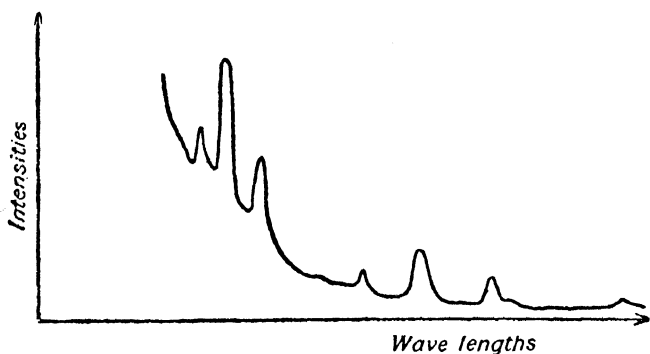


FIG. 19.

photographs of Plates 1, 2, and 5, so that the method of the rotating crystal is now usually employed. Indeed, absorption discontinuities (bromine, silver, and copper) were obtained for the first time by using this method (de Broglie [4]).

Moseley, whose experiments were published shortly after those of de Broglie, used limited portions of the spectrum obtained with a fixed crystal, and in this way discovered the fundamental law which bears his name.

**2. The ionisation method.**—Fig. 20 shows the arrangement of the tube and spectrometer. The rays issuing from the anticathode A traverse two slits F and F', are reflected

at the crystal C, and enter the ionisation apparatus by the slit F''.

The apparatus can be used in several ways :—

(a) The crystal C remains fixed, the slits F and F' are opened so that a pencil of fairly large angle is obtained, and the ionisation chamber and its slit are moved to receive successively the rays reflected at the different angles of a small spectral region ; the slit F'' may be very narrow.

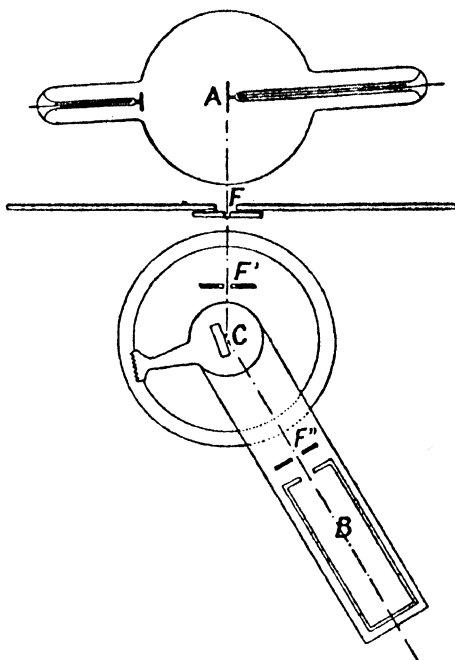


FIG. 20.

(b) The slits F and F' are closed so that a narrow pencil results, and the crystal is moved step by step, the ionisation chamber being stationary and the slit F'' wide open. In general, this second method is the better.

It was by using this spectrometer that Sir William Bragg and his son carried out their beautiful researches on crystal structure, and gave, for rhodium and platinum, the first examples of high-frequency spectra. Moseley and Darwin,

Duane and his collaborators, A. H. Compton, and other physicists have extended the ionisation method with success to the measurement and investigation of spectra. Webster has applied it, as has been mentioned in Chapter IV, to the examination of the connection between the excitation of spectra and the energy of the cathode rays in the tube used as the source of X-rays.

The photographic method, however, is preferable in a very large number of cases. It is true that Bragg's method gives a measured value for the various portions of the radiation, but the relation between the currents observed and the intensities of the rays is not a simple one.

The arrival of the rays in the chamber B produces ionisation in the gas present. It is known from C. T. R. Wilson's beautiful experiments that this ionisation is not due directly to the X-rays but to secondary  $\beta$ -rays which the X-rays detach from the molecules of the gas which they encounter. These  $\beta$ -rays produce a large number of pairs of ions along their sinuous paths, the lengths of which depend on the initial energy of the rays and on the nature and the pressure of the gas.

At the same time as they expel these electrons the X-rays cause the molecules of the gas to emit their characteristic radiations (at least those which are such that the frequency of the corresponding absorption limit is less than that of the incident rays) and these radiations in turn give rise to the emission by the gas of radiation possessing a smaller quantum, as is clearly shown by the photoelectric phenomena of X-rays (Chap. VI).

The production of ions in a gas is thus principally a selective phenomenon, depending on the frequency of the incident rays, the frequencies of the absorption discontinuities of the atoms which constitute the gaseous molecules, and on the corresponding absorption coefficients.

A vapour containing elements of high atomic weight, e.g. methyl bromide or iodide, will be suitable for use in the case of rays of low intensity if the frequency is greater

than that of the absorption discontinuity of bromine or iodine. Naturally, however, the ionising power of every radiation will change with the frequency, and will be subject to sudden and large variations as this frequency passes through the absorption discontinuities of the gas used. Sulphur dioxide has also been employed, air alone would generally produce effects which are too small.

The extent to which the rays under examination are absorbed depends also on the dimensions, the length and the diameter, of the ionisation chamber. If the chamber is not very large, the penetrating rays will be absorbed to a less extent than the others; in addition it is necessary to take into account the absorption of the secondary rays excited. This is sufficient to give an idea of the complex character of the problem of connecting the intensity of the ionisation observed with the energy possessed by the incident beam.

If there be added to these difficulties the absorptions of the radiations in the anticathode and in the walls of the tube, and the question of the coefficient of reflection of the crystal, it will be seen that the ionisation method only provides a photometric analysis of the beams of X-rays if many and difficult corrections be applied to the results obtained.

Details concerning the construction of various forms of ionisation spectrometers, which have been brought to a high degree of perfection by these authors, will be found in the papers by Webster, Duane, Cooksey, and Dershem (*Phys. Rev.*, 1917 to 1921). A. H. Compton [41] has constructed a self-recording spectrometer. Uhler [42] has examined in detail the geometrical properties of the diffraction images.

**3. The photographic and rotating crystal method.**—The essentials of the arrangement used in this method are shown in Fig. 21. The apparatus can be constructed by using several stands capable of sliding along the rail of an optical bench, a slit A, a crystal OC, the axis of rotation of which must lie in the reflecting surface, and a photographic dark slide D. In order that the images may be in focus on the

photographic emulsion this must be tangential to the focal cylinder of radius  $OD = DA$ .\*

As the crystal rotates, the different parts of the continuous spectrum are recorded on the film, the values of the wave-lengths being ascertained by reference to the position, indicated by sudden changes in intensity, of absorption discontinuities. Small imperfections of the crystal, which are very disturbing without this rotation, disappear completely. To avoid spurious effects, and at the same time to shield the plate, a screen, in which is a slit arranged to follow the movement of the reflected ray, may be placed in front of the plate.

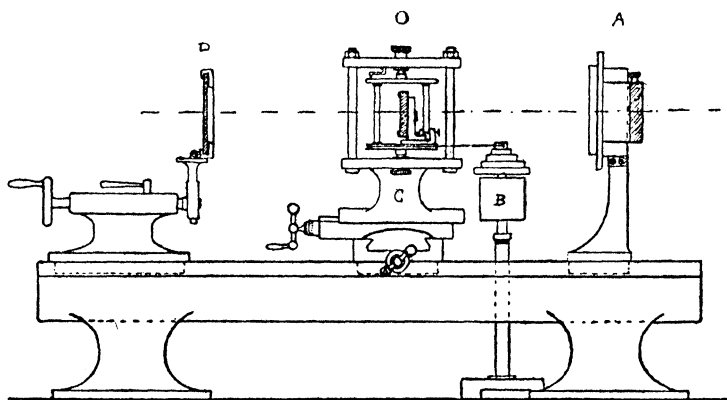


FIG. 21.

The photographs obtained are really impressions of the displacement of a spot of Laue's diagram ; the spectrum for a cleavage face is the most intense, but others are also obtained, as can be seen from the first photographs published by M. de Broglie (Fig. 1, Plate 4), the faces of the crystal which belong to the same vertical zone as the cleavage face used (i.e. which are also planes parallel to the axis of rotation) giving rise to spectra situated on the same horizontal line as the principal spectrum. In general, this effect is not very confusing.

\* In the figure, B is a clockwork arrangement (from a self-recording barometer) used for rotating the crystal.

The component parts of the preceding apparatus can be arranged in other ways adapted to the particular kind of research undertaken. The properties of the rays and of the crystals, above all the absorption of the rays, necessitate the modification of the apparatus according to the regions to be examined. The spectrograph shown in Fig. 4, employed by M. de Broglie, A. Dauvillier, etc., is suitable for X-rays of medium wave-length (0.2 to 3 Å.) but for very short or very long rays different apparatus is necessary.

The use to which Siegbahn, of the Lund Institute of Physics, has been able to put the spectrography of X-rays by the photographic method is well known.

**4. Special arrangements for rays of short and of long wave-length.**—Radiations of wave-length less than 0.1 Å. can only be investigated with difficulty by means of crystalline diffraction.\* Those which extend from 0.1 to 0.4 Å. are characterised by a very large penetrating power and a very small angle of selective reflection, even though crystals with small reticular distances be employed.

The penetration of the rays into the crystal deprives the external surface of its exact significance as the reflecting plane and removes the effective reflecting surface into the interior of the crystalline mass. This involves an error in the calculation of the angles which is the more important the less the quantity to be measured. Moreover, measurements are difficult when the glancing angle is too small.

Sir Ernest Rutherford [5] has constructed an arrangement specially suitable for the spectrography of rays of short wave-length and has used it to examine  $\gamma$ -rays of small and of medium penetration.

If a thin and fixed crystal of rock salt is placed perpendicular to the path of a slightly diverging pencil of rays (Fig. 22), there are reticular planes such as MN parallel to the axis of the pencil. These act as reflecting planes so that, if  $\alpha$  is the angle of selective reflection of the radiation

\*See, however, Chapter VI, Kovarik.



employed, one ray of the pencil which makes this angle with the axis will be reflected along the path REOB. Thus if the source is a slit, a series of black lines will be obtained on a plate placed at  $BB^1$ . The prolongations of the paths of the rays before reflection will meet the plate at  $AA^1$  and, as the energy of the radiation has been turned in another direction, the plate will be unaffected at these places and clear lines will be distinguishable. The central spot can also be screened off, thus eliminating the confusion which its intense blackening may cause.

Seemann [6] has modified this method by placing a narrow slit, situated on the axis of a goniometer, in contact with a thin crystal which can be rotated; in this case only the central rays are effective.

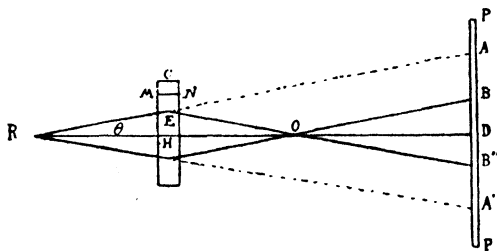


FIG. 22.

Siegbahn and Jönsson [7] have applied this arrangement to the measurement of absorption limits. A complete description of a form of spectrograph adapted to the investigation of short wave-lengths will be found in a paper by Siegbahn [8]. It consists of an arm, which can be rotated about an axis and to which are fixed several pieces of apparatus; the crystal is normal to this arm and the photographic plate is placed 50 cm. from the slit to which the crystal is attached (Figs. 23 and 24).\*

When the radiations have a wave-length greater than  $2 \text{ \AA}$ . their absorption by air at atmospheric pressure becomes considerable and this rapidly weakens them. It is then

\* In Fig. 23 the screen 2 is a slit for marking the zero of the plate. The thick screen near to it is for stopping undesirable rays.

necessary to work in a vacuum as with ultra-violet light. Between 2 and 3 Å., however, this complication can be avoided by placing glass tubes closed by thin celluloid mem-

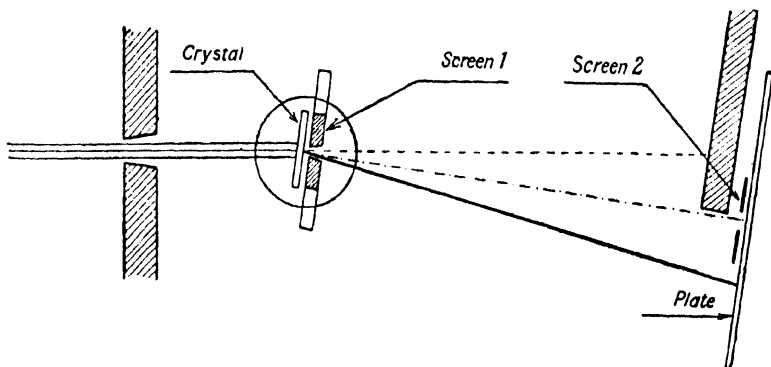


FIG. 23.

branes and filled with pure hydrogen at atmospheric pressure, along the path of the rays between the source and the crystal and between the crystal and the photographic plate. The low absorption coefficient of this gas enables work to be

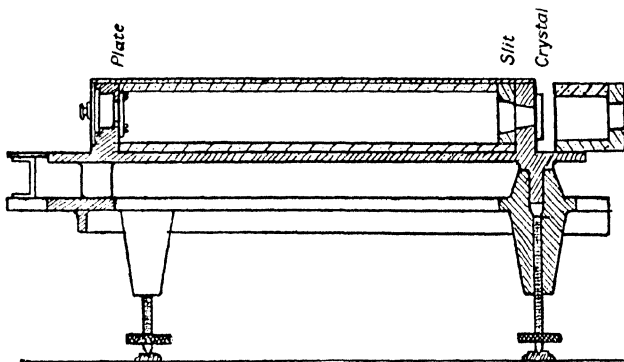


FIG. 24.

carried out with crystal-plate and crystal-slit distances of the order of 70 cm. even with these wave-lengths.

For still longer wave-lengths, however, a vacuum becomes indispensable, and, in addition, crystals which have as large reticular distances as possible, such as gypsum, must be

employed. It is well known that it is the upper limit of reticular distances compatible with cohesion which limits the region of crystalline diffraction at about  $12 \text{ \AA}$ .

Moseley [9] and then Siegbahn and his collaborators, Malmer, Friman, Stenström, Fricke, etc., have worked with vacuum spectrographs.

Stenström and Fricke [10] in particular, have described in detail the arrangement of the apparatus which they employed. It consists of an X-ray tube attached to an airtight case which contains the crystal and the plate, an

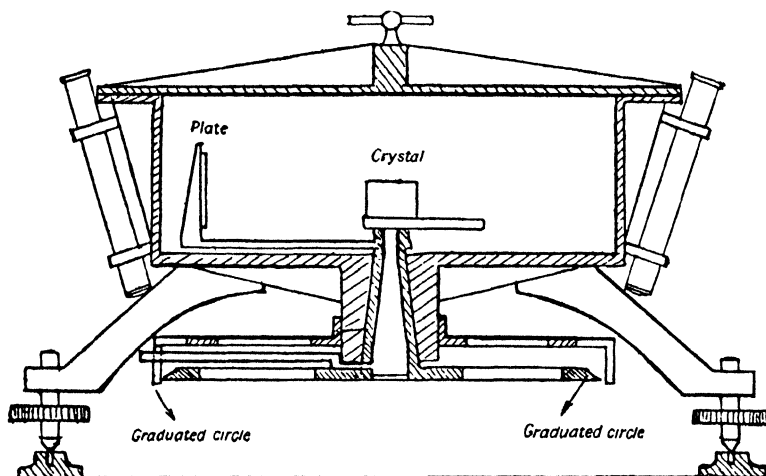


FIG. 25.

extremely thin membrane separating the very high vacuum in the tube from the slightly lower vacuum in the spectrograph itself. The crystal can be moved from outside the tube by means of accurately adjustable verniers without alteration of the vacuum.

Fig. 25 is a diagram of the general arrangements by which this angular displacement can be obtained. The central axis carries a double cone, one of the cones being used to measure the rotation of the crystal, and the other that of the arm to which the photographic plate is attached. The tube producing the rays (not shown in the figure) which is

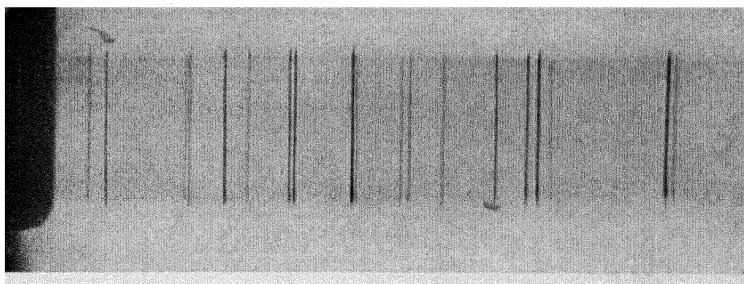


FIG. 1.—L SPECTRUM OF PLATINUM ANALYSED BY A ROTATING SHEET OF MICA  
(Low Dispersion; numerous successive orders)

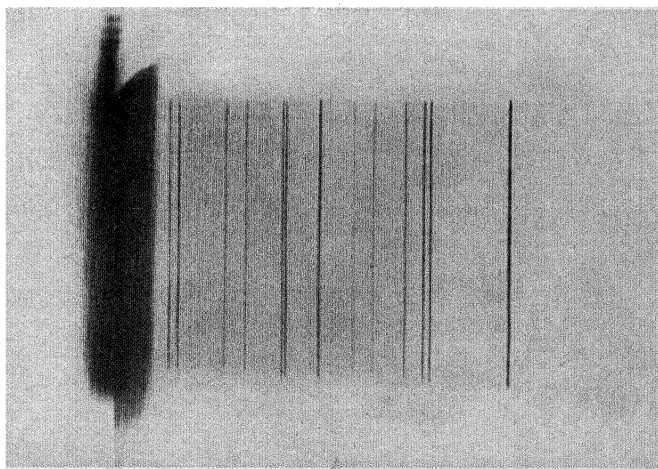


FIG. 2.—L SPECTRUM OF PLATINUM ANALYSED BY A CURVED SHEET OF MICA

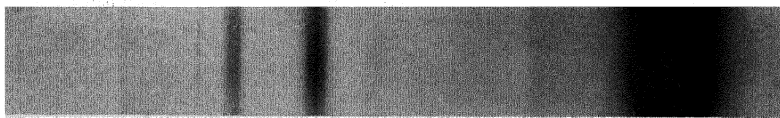


FIG. 3.—SPECTRUM OBTAINED BY THE PASSAGE OF A BEAM OF X-RAYS (L SPECTRUM OF PLATINUM) THROUGH A SHEET OF PLATINUM



also made of metal, opens directly into the interior of the spectrograph. The angles are measured by Siegbahn's method which will be described in paragraph 8.

Interesting forms of spectrographs and spectrometers have also been constructed by Seemann.

**5. Curved crystalline sheets.**—Cylindrical reticular surfaces, on which the beam of X-rays can be incident at all angles, can be made from flexible crystal such as mica. In this way an extended spectrum in which the lines are very fine (Figs. 1 and 2, Plate 5) can be photographed (de Broglie and Lindemann) [11] at a single exposure. The apparatus

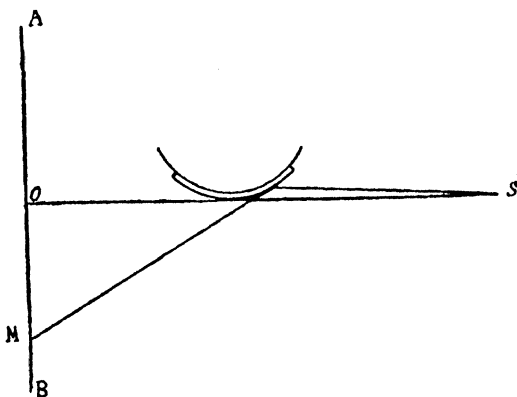


FIG. 26.

is very simple ; all that is necessary is a cylindrical wooden "form," of 15 mm. radius, on which is gummed a sheet of mica obtained by cleavage (Fig. 26).

The plate may be situated either on AB or in the plane of the figure ; it shows then the actual paths of the rays and the different pencils reflected at the cylindrical surface.

If the mica sheet were exactly in the form of a logarithmic spiral, the source of the rays being at the pole, all the surface could be utilised since the angle at which any ray was incident on it would be constant (de Broglie and Lindemann).

Measurements by using curved sheets of mica have been made by Rohmann [12], Gorton [13], and Siegbahn [14].

D. L. Webster [43] has used a curved mica sheet with a large radius of curvature (40 and 80 cm.) in his researches on the lines of the L series of the heavy elements.

Yoshida [45] has also investigated the L spectrum of tungsten with an apparatus of the same type, and he has been able to follow the reflections of some of the lines up to the seventh and even the tenth order.

Certain crystals, such as rock salt, can be bent under the action of heat, but, as Cermak [15] and Joffé [16] have shown, in these cases the whole of the crystal lattice is not curved but the crystalline mass is distorted by a slipping of the planes parallel to certain faces.

In connection with the reflection of a monochromatic beam of rays at a cylindrical mica surface, Gouy [17] has pointed out that if a source is placed on the axis of the cylinder it will produce at the conjugate point of this axis a real image having exactly the same properties as optical images. Darbord \* has obtained these images by means of thick curved sheets. In this case the position of a source can be chosen so that after reflection the rays of a diverging pencil meet again at a point.

**6. Measurements of wave-length.**—The evaluation of wave-lengths is accomplished by means of Bragg's formula, using the generally admitted values for the reticular distances of the crystals ( $2.814 \cdot 10^{-8}$  cm. for rock salt and  $3.082 \cdot 10^{-8}$  cm. for calcite), and measuring the angle of selective reflection.

The latter operation is not always easy. By measuring the deviation on each side and by determining the distance from the axis of rotation of the crystal to the plane of the plate  $\alpha$  can be obtained from the relation

$$\tan 2\alpha = \frac{AA^1}{2OC} \text{ (Fig. 27),}$$

but the measurement of OC, a distance which separates a plane from an axis of rotation, may be difficult. Uhler and

\* *Journal de Physique*, 1922, p. 218.

Cooksey [18] have overcome this difficulty by withdrawing the plate by a distance  $DC = d$ , which is easy to measure, and finding  $\alpha$  by the relation

$$\tan 2\alpha = \frac{EB}{EA} = \frac{BB' - AA'}{2d}.$$

This method has the advantage that if the plate is withdrawn for different values of  $d$  it ensures that the axis of rotation is correctly situated with respect to the reflecting face of the crystal. The errors resulting from this defect are, in fact, a function of the distance of the crystal from the plate

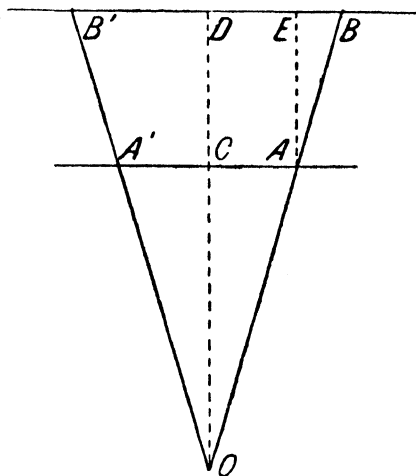


FIG. 27.

and rapidly diminish as this increases. Their relative importance can become considerable for small angles.

The crystal can also be mounted on an accurately graduated circle and a method given by Siegbahn employed [19] (Fig. 28). The camera arm of the instrument is adjusted to a value  $\alpha_1$ , approximately equal to the angle  $\alpha$  which it is desired to measure accurately; the line is then photographed and will be in a certain position on the photographic plate. The arm is next turned through an angle  $4\alpha_1$ , and the crystal through  $180 + 2\alpha_1$ , and the same plate re-exposed: the two lines on the plate will then coincide if  $\alpha_1$



is exactly equal to  $\alpha$ . In general there will be a small separation between the two lines and if this is measured by a micrometer  $\alpha$  can be obtained from  $\alpha_1$ .

The lines are very fine and can be measured with great accuracy; for example, Siegbahn [19a] when measuring a copper line using different specimens of calcite found values of  $\alpha$  differing only by some tenths of a second of arc ( $14^\circ, 42', 0.8''$  and  $14^\circ, 42', 0.4''$ ), which led him to give for the wave-length of this line the value  $1.537302 \cdot 10^{-8}$  cm.

It should be noted, however, that, as in optical spectroscopy, the lines are not always simple and they may be of

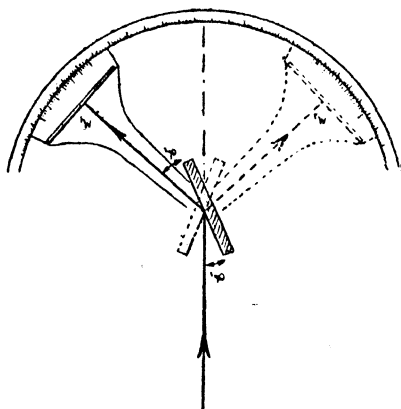


FIG. 28.

appreciable breadth. A glance at the tables given in Chapter IV shows that the numerical results obtained by various observers still differ appreciably.

Moreover, it should not be forgotten that the calculation of the wave-lengths involves the reticular distances of the crystal employed. In the case of calcite Siegbahn [44] assumes a value of  $d = (3028.3 \pm 2.2) \cdot 10^{-11}$  cm., obtained from the formula

$$d = \left( \frac{MeE}{2\rho VSc} \right)^{\frac{1}{2}}$$

by using the following data :—

$M$  = Molecular weight of  $\text{CaCO}_3 = 100.075$ .

$\rho$  = Density of calcite  $= 2.7125 \pm 0.0015$ .

$E$  = Electrochemical equivalent of silver  $= 0.00111827$ .

$V$  = Volume of elementary rhombohedron  $= 1.0963 \pm 0.0007$ .

$e$  = Electronic charge  $= (4.774 \pm 0.005) \cdot 10^{-10}$  E.S. units.

$S$  = Atomic weight of silver  $= 107.88$ .

$c$  = Velocity of light  $= 2.9968 \cdot 10^{10}$  cm./sec.

$d$  is thus known with an accuracy less than that of the angular measurements.

The wave-lengths of the lines can be measured by means of their spectra of higher orders and thus there is revealed a systematic tendency, which has not yet been clearly explained. The measurements of the second and third orders always yield values of  $\alpha$  which are *slightly less* than those given by the first order. For example, in the case of the copper line cited above, whilst the mean of the first order measurements is  $14^\circ, 42', 0.6''$ , within less than one second, the second and third orders give values of approximately  $14^\circ, 41', 55''$ .

Recently Siegbahn [20] has discussed the possible causes of this divergence, of which Ewald has suggested a theoretical explanation [21].

With such a degree of accuracy it is necessary to take into account the thermal expansion of the crystal; this will affect the value of the reticular distance.

**7. Dispersion, resolving power.**—As with optical grating spectra the dispersion varies with the grating constant (the reticular distance) and with the order of the spectrum.

The resolving power increases with the distance between the crystal and the slit which is equal to the distance between the crystal and the photographic plate, since as Bragg's focal theorem indicates, the image of the slit is always equal to the slit. In practice it is found impossible to avoid a certain broadening of the spectral lines as the length of the

spectrograph increases. Nevertheless the resolving power increases with this length.

Spectra have been obtained with a distance of 4 metres between the slit and the photographic plate, and have permitted the wide separation in the second order of the two components of the  $\beta$  line of the K spectrum of tungsten, platinum, and rhodium (M. de Broglie [22]).

To a first approximation X-ray spectra are normal spectra, the distance of a line from the central point being proportional to the wave-length of the line. Since  $x = k\lambda$ , it follows that  $\Delta x = k\Delta\lambda$ , or converting to frequencies,  $\nu = \frac{c}{\lambda}$  and

$$\Delta x = -kc \frac{\Delta\nu}{\nu^2}.$$

Thus the separation of two lines, the difference of frequency between which is constant, rapidly diminishes as the frequency increases. For this reason, certain fine structures are usually more readily distinguishable in the low frequency region.

In this connection it may be mentioned that in the magnetic spectra of secondary  $\beta$ -rays the distance of the lines from the origin is, on the other hand, directly proportional to the square root of the frequency\* so that the components of higher frequency lines can be more easily observed than with diffraction spectra. For example, a separation of 5 mm. between the  $\alpha_1$  and  $\alpha_2$  lines of the K series of tungsten is easily obtained, such a separation in the first order diffraction spectrum being possible with a rock salt crystal only if the photographic plate were more than 5 metres from the slit.

**8. The photography of absorption spectra.**—When absorption spectra are to be examined, a screen of the substance to be examined is placed between the source and the photographic plate. This screen can be situated either in front

\* Actually the law of dispersion is more complex than this and depends on the strength of the field employed, but only the general trend of the dispersion is indicated here.

of the slit, when the surface required is greatly reduced, or in the immediate neighbourhood of the photographic plate, this being advantageous when it is desired to juxtapose several spectra.

The bromine and silver of the emulsion exert their selective absorption in the sensitive layer itself and this is indicated by the well-known reversed bands (Fig. 3, Plate 1). If another substance is placed in contact with the emulsion it produces, to a less extent, a similar effect ; a sheet of tin, for example, placed next to the gelatine will give the tin band reversed (having the darkest part on the short wave-length side). This effect is due to the secondary radiations excited in the tin screen, and chiefly to the secondary  $\beta$ -rays, as can be shown easily by their absorption if a very thin sheet of aluminium foil is interposed between the screen and the emulsion.

The energy absorbed by the screen from the incident radiation is re-distributed in all directions. If the distance between the screen and the sensitive layer is increased the latter is only reached by a very small fraction of the secondary radiations, so that the absorption effect predominates and the band recorded in the spectrum assumes its normal aspect of an absorption band in which the darkest part is on the long wave-length side of the absorption limit.

The absorption effect can be produced if the substance is in any position along the path of the rays, in the anticathode itself, in the walls of the tube, in the substance of the analysing crystal (which the rays penetrate to an appreciable distance), in the colouring matter (antimony sulphide) of the black paper which protects the plate, and so on.

The absorption in the anticathode gives rise to the following effect : when the anticathode itself, viewed sideways so as to look like a thin line, is used as the source, the emerging rays which graze the emitting surface always exhibit absorption spectra, so that the spectrum obtained is limited on the high frequency side by the  $\gamma$ -line of the K series of the anticathode.

The absorption in the analysing crystal has often been noted when the region under examination embraces a discontinuity characteristic of the elements composing the crystal.

**9. The use of reinforcing screens.**—The action of reinforcing screens (M. de Broglie) [25] depends on phenomena of the same nature as those just mentioned. Thus the bands due to the bromine and especially to the silver of the emulsion make the plate specially sensitive to rays of short wave-length. The action of the screens, however, is still more complex. A screen frequently employed is composed of a thin layer of calcium tungstate placed in contact with the emulsion. The action of the incident rays produces two different kinds of phenomena in the substance of the screen. The first is the emission of secondary X and  $\beta$  radiations, which is an atomic property of the substance and does not depend on its physical or chemical state, the method of preparation, its crystalline structure, etc. ; there is also a luminous fluorescence which does depend on these conditions and is not produced, for example, by a mixture of tungstic acid and calcium oxide.

Under the conditions usually obtaining when the screens are used it is the latter which has the greater action on the emulsion.

The reinforcing action increases very rapidly with the penetration of the rays. Whilst it is scarcely perceptible in the middle region of the L rays of tungsten ( $\lambda = 1.2 \text{ \AA.}$ ) it becomes appreciable at about  $1 \text{ \AA.}$  and grows very rapidly without any sudden alteration till the K limit of tungsten is reached ( $\lambda = 0.179 \text{ \AA.}$ ). A sharp increase of reinforcing power then occurs which produces on the emulsion a reversed band corresponding to this wave-length. The emission of luminous rays by the screen also appears to depend on the critical absorption discontinuity of the heavy metal which the screen contains.

On account of the increased reinforcement of short wave-lengths the spectra of the higher orders \* of these regions

\* The excitation of the high-frequency region can be avoided by limiting the voltage applied to the tube.

tend to mask the first order spectrum of the longer wavelengths if a reinforcing screen is used when photographing an extended spectrum. Similarly, the absorption bands due to the bromine or silver of the emulsion become much less prominent so that the aspect of the spectrum taken under these conditions is completely altered.

For a short spectral region of penetrating rays ( $\lambda$  less than  $0.5 \text{ \AA.}$ ) the time of exposure can be very much reduced with the aid of a good screen, without greatly affecting the sharpness of the lines, if the grain of the screen is sufficiently fine.

The reinforcing power of a screen probably also depends to some extent on the intensity of the radiation examined ; perhaps there may be a limit to the reinforcing action.

**10. Microscopic crystals and crystalline powders.**—At the time of their first researches in 1912, Laue, Friedrich, and Knipping observed that the crystalline diagrams obtained when a beam of X-rays traversed a large crystal disappeared when the lattice was destroyed by powdering the crystal. Actually this is not quite the case ; the spots of the crystalline diagrams naturally disappear when the reticular planes in fixed directions to which they are due in a large crystal are destroyed, but the pulverisation of a large crystal results in the production of a large number of microscopic crystals and not in an amorphous powder. These small crystals, if packed at random, are equivalent to a crystal with planes in all directions, so that the diffraction phenomena retain only a symmetry of revolution round the pencil of X-rays, and if a photographic plate is placed normal to the direction of the pencil it gives rise to a series of circular halos. If the X-rays are monochromatic, each crystalline face will give a characteristic circle (if attention be confined to the first order). The principal faces of the system to which the crystalline substance belongs will thus be analysed, even if the substance is apparently an amorphous powder.

If the beam of X-rays has a complex line spectrum, each

of the lines will give rise to a series of circles, but if one crystalline face has a greater reflecting power than the others, to a first approximation it only will be effective and will give the line spectrum of the incident radiation.

Friedrich [24] obtained these halos, using such substances as bees-wax, amber, paraffin, and Canada balsam. It may be that some of these substances have a micro-crystalline structure.

The phenomena characteristic of truly amorphous substances will be considered later.

Hupka [25] observed that when metallic sheets are traversed by a beam of X-rays Laue spots, which are more or less diffuse, are produced, indicating a crystalline structure.

De Broglie [26] has shown that the spectrum of the incident rays can be obtained even when a beam of X-rays limited by a slit merely passes through a sheet of platinum, gold, or silver (Fig. 3, Plate 5). In this spectrum the silver and the bromine bands and the principal lines of the metal of the anticathode can be distinguished, which allows the calculation of the constants of the sheet by means of the dispersion of the spectrum.

These investigations demonstrated the possibility of examining crystalline powders by means of their diffraction phenomena without much more difficulty than in the case of large crystals. The internal crystalline structure of metals is particularly interesting. When the small crystals in the interior are in complete disorder halos and not spots are obtained. The gradual appearance of spots which become more and more distinct, enables us to follow the phenomena of internal crystallisation, and the importance of this in metallography is well known.

Debye and Scherrer [27] and Hull [28] in 1916 and 1917 independently developed similar methods of obtaining crystalline diagrams with powdered crystals.

It is sufficient to place a photographic plate normal to a pencil of X-rays and a small quantity of the powdered crystal between the source and the plate. A system of



FIG. 1.—APPARATUS FOR X-RAY SPECTROGRAPHY

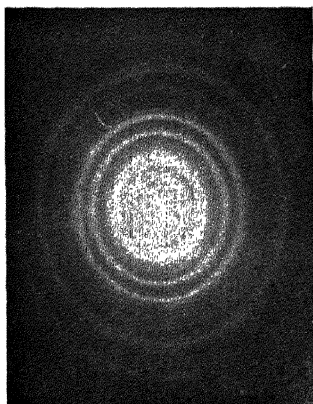


FIG. 2.—DIFFRACTION HALOS PRODUCED BY THE PASSAGE OF X-RAYS THROUGH POWDERED CRYSTALS

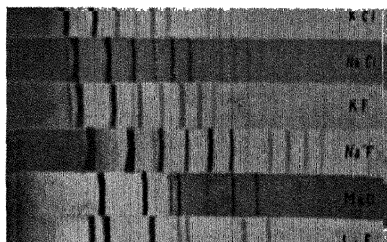


FIG. 3.—DIAGRAMS OF POWDERED CRYSTALS (Hull)

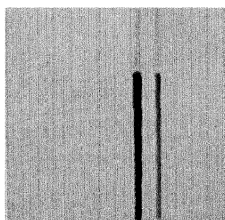


FIG. 4.—SPECTRUM OF K-RAYS (WIDE SLIT) OBTAINED BY SECONDARY RAYS





halos is then obtained, the arrangement of which varies with the radiations and with the substance employed. Such systems are illustrated by Figs. 2 and 3 of Plate 5.

The important information concerning crystalline structures which has been obtained in this way will be found in another volume of this series of monographs.\*

Hull's researches have been developed chiefly with a view to obtaining "face patterns" of various salts. These are quite characteristic and by this means specimens can be directly analysed, if the same radiation (as simple as possible) is always employed. A practically monochromatic radiation can be obtained by means of a tube with a molybdenum anticathode capable of carrying a strong current at 30,000 volts, the radiation being filtered through a zirconia screen containing 0.05 gram,  $\text{ZrO}_2$  per square cm.

Hull has also applied the diffraction phenomena exhibited by crystalline powders to investigations into the structures of metallic crystals.\*

The influence of rolling and annealing on a number of metals, Al, Cd, Cu, Zn, Pd, Tl, Ag, and Sn, has been studied by S. Nishikawa and G. Asahara [29], who have been able to discover transformation points in the cases of thallium and tin.

Kahler [30] has examined the structure of the very thin films formed by the condensation of bismuth and silver vapours on cooled surfaces, and of films formed by cathodic spluttering. The former do not appear to possess the crystalline structure which is very evident in the case of the latter.

Miss Andrews [31] has applied Hull's method to the examination of the various iron-nickel, iron-cobalt, and copper-zinc alloys, and has shown that under certain conditions solid solutions are formed, in which are characteristic crystalline forms.

Several investigators, Becker [32], Jancke [33], Ettisch, Polanyi [35], and Herzog [36], have studied the characteristic

\* See the monograph by M. Mauguin which is devoted to the crystallographic applications of X-rays.

phenomena which are presented by finely drawn metal threads. Their Laue diagrams, instead of showing halos, are composed of more or less well-defined isolated spots which indicate a less degree of disorder, and, strangely enough, the same phenomenon has been found with cellulose. The diffraction patterns again become halos when the incident rays are parallel to the direction of the fibres.

Finally, Sir William Bragg [37] has recently attacked the study of powdered crystals by means of an ionisation spectrometer. Special apparatus for the photographic examination of powdered crystals have been described, notably by Wheeler P. Davey [38] and Assar Hadding [39].

**11. Diagrams of non-crystalline substances.**—In reality the phenomena just mentioned only present a particular case of the ordinary Laue diagrams which are characteristic of matter in the crystalline state. Substances to which it does not appear possible to attribute a crystalline structure in the ordinary sense of the word nevertheless appear to have the power of giving rise to diffraction rings.

In paragraph 4 of Chapter II reference was made to Debye's theory which predicts these rings even when a beam of X-rays traverses an irregular assemblage of atoms, on account of the fact that in each atom the distribution of the electrons has a structure. Debye has announced that such phenomena can be observed when X-rays pass through isotropic liquids like benzene. Debierne [40] has obtained rings with various liquids, mercury, methyl iodide, methylene iodide, benzene, bromobenzene, etc., and with some mixtures. He has explained this result differently from Debye by assuming that diffraction centres, either atoms or molecules, exist in these liquids, which though distributed at random, satisfy the condition that neighbouring centres have always the same distance between them, like the centres of small spheres in contact. He gives the following explanation on this assumption :—

“ Let us consider two neighbouring centres in any position with respect to the direction of the incident beam. The

waves diffracted by these two centres will interfere, and in the plane containing the incident ray the addition of the amplitudes will take place in a direction making an angle with the ray which can be easily calculated. But it is seen immediately that this angle has a minimum value given by the equation—

$$\sin \frac{\alpha}{2} = \frac{\lambda}{2a}$$

$\lambda$  being the wave-length of the radiation and  $a$  the fixed distance between the centres. It follows that for every radiation an important part of the diffracted energy is concentrated in the neighbourhood of the direction of the minimum."

Keesom and de Smedt [46] have studied the interference figures presented by certain liquids and liquefied gases; from their results they have obtained the following values of the mean distance  $a$  between the diffracting molecules of these substances :—

Oxygen . . . . .	4.0 Å.
Argon . . . . .	4.0
Benzene . . . . .	6.0
Water . . . . .	3.7
Ethyl alcohol . . . . .	4.9
Ethyl ether . . . . .	5.7
Formic acid . . . . .	4.5

Experiments carried out on the substances called "liquid crystals" have generally yielded negative results; however, the investigations of M. de Broglie and E. Friedel [47] on the oleates have given photographs showing concentric rings which correspond to the reflections of various orders. The measurement of the diameters gives for the distance between the reflecting planes the value 43.5 Å., which is remarkable on account of its size. We shall not dwell any longer on these questions, the investigation of crystals by means of X-rays being outside the scope of this book.

These examples show that the information to be obtained from the diffraction of X-rays is not confined to the structure

of crystals, and can assist us to make still further progress in our knowledge of the properties of matter. In particular it is desirable that the nature of the diffraction phenomena which homogeneous liquids appear to exhibit, and which are still rather obscure, should be examined and elucidated as rapidly as possible.

### SOURCES OF X-RAYS

**12. New hot cathode tubes.\***—(1) *Coolidge tubes*.—These tubes are characterised by a very low pressure, so low that ionisation phenomena play no part in their action, and by the cathode which consists of a plane spiral of tungsten wire raised to incandescence by an auxiliary current, and situated at the centre of a concentrating cup, which is sometimes cylindrical and sometimes hemispherical. The anticathode is either a mass of forged tungsten (standard tube), self-cooled by thermal radiation, or a tungsten pastille encased in a mass of copper, which is cooled either by conduction to a radiator outside the tube attached to the copper (radiator tube), or by the circulation of water.†

Water-cooled Coolidge tubes have withstood energy inputs of 10 kilowatts under an applied voltage of 100 effective kilovolts, the anticathode being cooled in the same way as a motor-car engine, the same arrangement being employed. Elongated Coolidge tubes have recently been constructed capable of being run at 200,000 volts.

(2) *The Lilienfeld tube*.—This tube also depends on the emission of electrons by an incandescent cathode F which is at a temperature sufficiently high for an excess of electrons to be always emitted (Fig. 29). Some of these are used to produce the cathode beam being attracted by an auxiliary

\* See A. Dauvillier, . . . *Rapport sur les tubes destinés à la radiographie profonde et leur rayonnement* (*Journal de Radiologie de Bruxelles*, 1921).

† The Coolidge radiator tube, in which one electrode only is incandescent during operation, can be used without a rectifier, itself acting as a valve, but it does not support more than 50,000 volts.

field of several thousand volts, produced between the glowing filament and a hollow aluminium cylinder C (the pierced cathode) which points towards the anticathode. Their bombardment of the interior of this cylinder ionises the metal and causes it to become the source of a larger number of slow-moving electrons. These emerge from the cylinder into the principal field which is applied between this electrode and

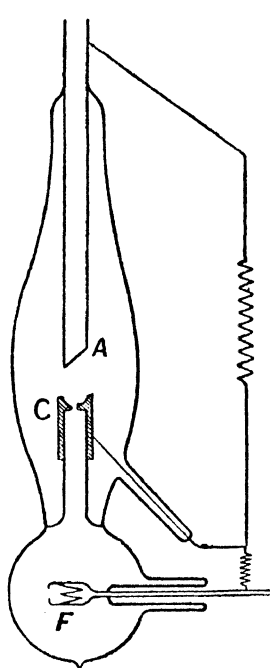


FIG. 29.

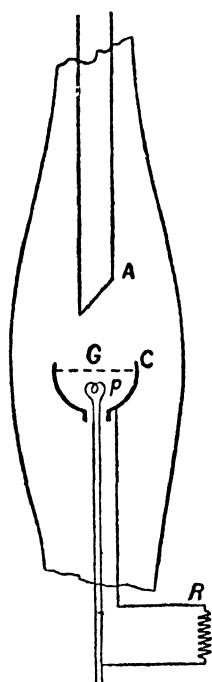


FIG. 30.

the anticathode A, and constitute the cathode rays. The intensity of the beam is regulated by the magnitude of the auxiliary field, whilst the velocity of the electrons of which it is composed is adjusted independently by the potential difference applied to the second circuit.

This tube was constructed by its inventor to give high instantaneous electronic densities at the focus when used with sinusoidal or pulsatory voltages. In order to utilise

only the crest of the voltage waves the difference of potential applied to the filament heating circuit is adjusted so that it only slightly exceeds the critical potential required to light up the filament. The waves applied to the principal circuit CA, and to the auxiliary circuit FC, being of the same shape and in the same phase, the tube only lights up at the crest of the voltage and gives a radiation nearly as homogeneous as that yielded by a "hard" gas tube run with the same voltage wave.

The cathode of the Lilienfeld tube is made of platinum ; if the periodicity of the applied voltage be 500, it can take 8 milliamperes (mean) at 170 kilovolts (max.), provided that the anticathode is water cooled.

(3) *The Muller "electron" tube.*—In this tube (Fig. 30) the incandescent filament is contained in a metal cup C covered on the anticathode side by a grill of large mesh, G. This cup is insulated from the filament circuit but is connected with it outside the tube through a high resistance R. If this resistance were infinite the grill would become charged to a negative potential of several volts, the magnitude depending on the filament temperature, and even fairly large differences of potential between A and P would be incapable of drawing the electrons from the cup. On the contrary, if R were zero the grill would only act as a Faraday net and, its mesh being large, it would not greatly hinder the discharge. The object of the resistance R is to regulate the negative potential of the grill in such a way as to permit the principal field to extract a sufficient number of electrons to serve as the cathode beam at the instant that the voltage wave is at its maximum.

This tube has a platinum anticathode which is cooled either by the boiling or by the circulation of water. It is nearly 80 cm. long and can carry continuously 5 milliamperes at 220 kv. max.

4. *Special tubes for research purposes.*—A large number of arrangements have been employed in the construction of tubes intended for direct attachment to spectrographs.

Principally it has been desired to bring the anticathode near the walls of the tube; to avoid overheating, therefore, it is necessary to use water jackets. For example, Fig. 31 \* illustrates a metal tube of this type. In the case of soft rays the voltages may be low and so insulation is not difficult even with entirely metallic tubes. For higher

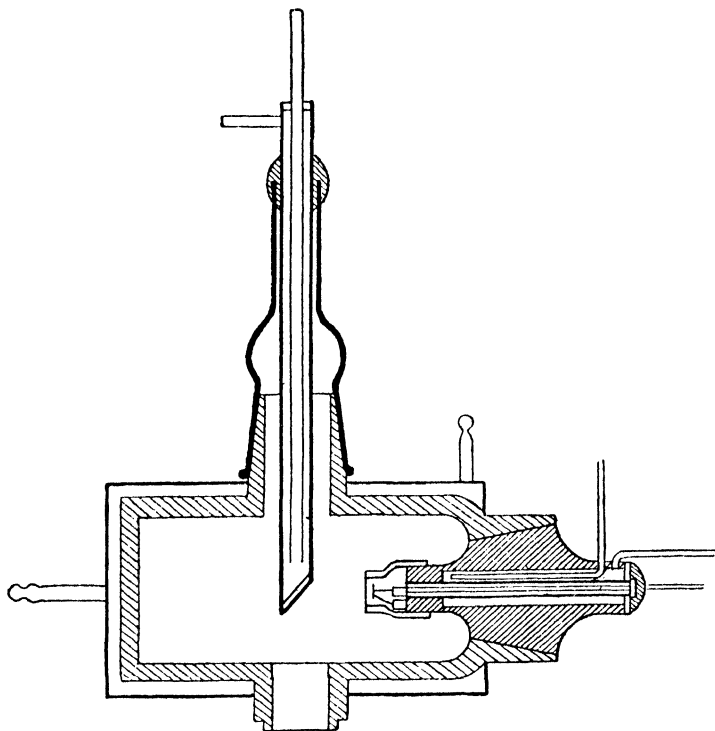


FIG. 31.

voltages Dauvillier † has described a well-thought-out quartz apparatus.

**13. Constant voltage apparatus.**—Great progress has been made by running tubes at constant voltage. This method of working does not lend itself to gas tubes, but is very well adapted for use with hot cathode tubes.

\* Taken from a paper by M. Siegbahn.

† *Journal de Physique*, 1922, p. 170.



Statical machines and high-tension accumulator batteries are not convenient in practice, but some time ago Villard described a statical arrangement by means of which a constant voltage can be obtained from an alternating current transformer. This method consists of charging a condenser through a valve. The invention of the kenotron, which is a perfect static valve, has made the method of practical value, and extended its application to very high tensions and powers.

The application of this arrangement to the voltage supply of X-ray tubes was carried out for the first time independently by Hull (*Phys. Rev.*, Jan., 1916, VII, p. 156) and Ledoux-Lebard and Dauvillier (*Comptes Rendus*, 1916).

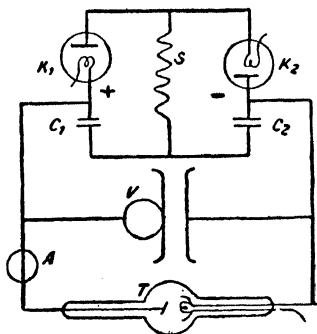


FIG. 32.

There are several modifications of the Villard arrangement. In the best of these, two inverse circuits, each consisting of a kenotron in series with a condenser  $C$ , are placed in parallel with the secondary  $S$  of a unipolar transformer (Fig. 32). Successive alternations charge the condensers in turn to the potential of the crest of the transformer voltage. The two capacities then discharge, in series, through the tube  $T$  which is thus supplied at a tension double that of the crest. A transformer giving 70 kv. (effective) combined with two 170 kv. (effective) kenotrons and two condensers capable of supporting 100 kv., will thus give 200 kv. static, measured by the Abraham-Villard voltmeter  $V$ . The extent of the

variation of the potential depends on the voltage, the frequency of the charging current, the capacity of each condenser, and is inversely proportional to the intensity of the current. For example, at 200 kv. with a frequency of 1000, capacities of 0.01 microfarad and a current of 50 milliamperes, the variations in the voltage are less than 2000 volts, i.e. the potential difference is constant to about one per cent.

## BIBLIOGRAPHY

1. W. H. and W. L. BRAGG, *Proc. Roy. Soc.*, 1913, 88, p. 428.
2. MOSELEY and DARWIN, *Phil. Mag.*, 1913, 2, p. 210.
3. M. DE BROGLIE, *Comptes Rendus*, 17 Nov. 1913, p. 924, and *Comptes Rendus*, 1913, 2, p. 1413; 1914, 1, p. 177.
4. M. DE BROGLIE, *Comptes Rendus*, 1914, 2, p. 1493.
5. SIR ERNEST RUTHERFORD and E. DA C. ANDRADE, *Phil. Mag.*, 1914, 2, p. 263.
6. SEEMANN, *Phys. Zeits.*, 1917, p. 242.
7. SIEGBAHN, *Phys. Zeits.*, 1919, p. 252.
8. SIEGBAHN, *Phil. Mag.*, 1919, 2, p. 639.
9. MOSELEY, *Phil. Mag.*, 1914, 1, p. 703.
10. SIEGBAHN and FRIMAN, *Phys. Zeits.*, 1916, p. 176.
11. M. DE BROGLIE and F. A. LINDEMANN, *Comptes Rendus*, 1914, 1, p. 944.
12. ROHMANN, *Phys. Zeits.*, 1914, p. 510.
13. GORTON, *Phys. Rev.*, 1916, 1, p. 334.
14. SIEGBAHN, *Phys. Rev.*, 1916, 2, p. 320.
15. CERMAK, *Phys. Zeits.*, 1917, p. 405.
16. JOFFÉ, *Phil. Mag.*, 1922, 1, p. 204.
17. GOUY, *Comptes Rendus*, 1915, 2, p. 765.
18. UHLER and COOKSEY, *Phys. Rev.*, 1917, 2, p. 645.
19. SIEGBAHN, *Phil. Mag.*, 1919, 1, pp. 601 and 647.
- 19a. SIEGBAHN, *Comptes Rendus*, 1921, 2, p. 1350.
20. SIEGBAHN, *Comptes Rendus*, 1922, 1, p. 745.
21. EWALD, *Phys. Zeits.*, 1920, p. 617.
22. M. DE BROGLIE, *Comptes Rendus*, 1920.
23. M. DE BROGLIE, *Comptes Rendus*, 1920, 1, p. 1053.
24. FRIEDRICH, *Phys. Zeits.*, 1913, p. 317.
25. HUPKA, *Phys. Zeits.*, 1913, p. 623.
26. M. DE BROGLIE, *Comptes Rendus*, 1914, 1, p. 333, and *Soc. de Phys. All.*, Feb. 1914.

27. DEBYE and SCHERRER, *Phys. Zeits.*, 1916, p. 277, and 1917, p. 291.
28. HULL, *Phys. Rev.*, 1917, 2, p. 661.
29. NISHIKAWA and ASAHARA, *Phys. Rev.*, 1920, 1, p. 38.
30. KAHLER, *Phys. Rev.*, 1921, 2, p. 210.
31. MISS ANDREWS, *Phys. Rev.*, 1921, 2, p. 245.
32. BECKER, *Zeits. für Phys.*, 1921, 5, p. 61.
33. JANCKE, *Zeits. für Phys.*, 1921, 5, p. 61.
35. POLANYI, *Zeits. für Phys.*, 1921, 5, p. 61.
36. HERZOG, *Zeits. für Phys.*, 1920, 3, p. 343.
37. SIR WILLIAM BRAGG, *Proc. Roy. Soc.*, June, 1921.
38. WHEELER P. DAVEY, *Jour. Opt. Soc. of America*, Nov., 1921.
39. HADDING, *Zeits. für Phys.*, 1920, 3, p. 369.
40. DEBIERNE, *Comptus Rendus*, 1921, 2, p. 140.
41. A. H. COMPTON, *Phys. Rev.*, 1916, 1, p. 646.
42. UHLER, *Phys. Rev.*, 1918, 1, p. 1.
43. D. L. WEBSTER, *Proc. Nat. Acad.*, 1920, p. 26.
44. SIEGBAHN, *Jahrbuch der Rad. und Elektr.*, 1922, 18, part 3, p. 251.
45. YOSHIDA, *Science Abstracts*, Feb. 1923, p. 67.
46. KEESOM and DE SMEDT, *Ann de la Soc. Scient. de Bruxelles*, July 1922, p. 338.
47. M. DE BROGLIE and E. FRIEDEL, *Comptes Rendus*, II, 1, 1923, p. 738.

## CHAPTER VI

### PART I

#### SECONDARY $\beta$ -RAYS DUE TO X-RAYS

**1. The X-ray photoelectric phenomenon.**—When X-rays are incident on a substance there arises a secondary corpuscular radiation which is composed of more or less rapidly moving electrons, and this constitutes the X-ray photoelectric effect.

The experimental data which will be given later appear to establish that the incident periodic radiation of frequency  $\nu$ , communicates the whole of its quantum to those electrons which form the radiation, giving them a kinetic energy equal to  $h\nu$ . These electrons are then torn from the atomic levels to which they belonged and emerge from the atom, losing energy in escaping equal to the work of extraction corresponding to the level.

The places vacated by the expelled electrons are filled by new corpuscles when the atom returns to its normal state, fluorescent X-rays being simultaneously emitted. The photoelectric phenomenon and the secondary X-radiation are due therefore to the same mechanism and one involves the other.

**2. Investigations on the magnitude and the distribution of the velocities possessed by the electrons emitted under the action of X-rays.**—A large number of investigations,\* the first of which dates back to 1900 (Dorn, Bestelmeyer, Becker, Innes, etc.) [2], have been devoted to the study of the photoelectrons emitted by substances exposed to X-rays,

\* See also Von Baeyer, Ladenburg, etc.

the existence of these electrons having been discovered by Sagnac. Measurements of the velocities of the electrons can be made either by stopping them by an opposing electric field or by deviating them by a magnetic field. The latter method is greatly to be preferred in practice on account of the very high value which must be given to the opposing potential difference in the former. The outstanding fact indicated by the early investigations was that the secondary rays possess a velocity of the same order of magnitude as that of the cathode rays in the tube producing the X-rays. Thus the cathode rays by striking the anticathode of the tube give rise to X-rays, and the latter when they encounter a substance cause the emission of photoelectrons which, in their turn have an energy comparable with the energy possessed by the cathode electrons in the tube.

This result is one of those which have helped to build up the quantum theory ; one of the tenets of this theory is, briefly, that a certain definite quantity of kinetic energy is carried by the periodic wave which constitutes X-rays, and this kinetic energy can reappear in the form of energy possessed by electrons in rapid motion.

By receiving the photoelectrons deviated by a magnetic field on a photographic plate, Dorn, Bestelmeyer, and Innes obtained a magnetic spectrum of the corpuscular emission velocities, but they did not observe anything on the plate except a fairly sharp limit on the high energy side, which indicated a more or less well-defined maximum velocity, and a continuous background extending to very much lower velocities.

Scarcely anything more could be done before the great advance which Laue's discovery started. It should be mentioned, however, that Beatty [3] exposed a silver radiator to the secondary X-rays from various metals (Fe, Ca, Zn, As), and measured the coefficient of absorption of the photoelectrons produced, by an ionisation method. Although the coefficient of absorption of a beam of electrons has not a very definite significance, even when the beam is homo-

geneous as regards velocity, which was not so in this case, these measurements showed that the absorption of the  $\beta$ -rays excited varied in the same sense as that of the exciting X-rays, or, as would be said to-day, that the velocity of the  $\beta$ -rays increased with the frequency of the exciting X-rays, a property which is in qualitative agreement with the quantum theory.

The following among more recent investigations should be noted :—

Robinson and Rawlinson [4] employed a photographic method similar to that which has been used to analyse the radiation from radioactive bodies. An arrangement of this kind will be described later.

Long exposures (at least 12 hours) were necessary in order to obtain appreciable photographic results, but the existence of a magnetic line spectrum was proved ; some of these lines appear to correspond, within the limits of experimental error, to the quanta of the fluorescent lines of the radiator, others to the quanta of the lines of the spectrum of the incident X-rays. More recently, Kang Fuh-Hu [5] has carried out similar experiments using a Coolidge tube, which is more powerful. After exposures of about 24 hours, with a silver radiator, he found lines which appeared to him to correspond, to an accuracy of 5 per cent., to the quanta of the lines of this metal. He also tried an interesting experiment ; he covered the silver radiator with a thin sheet of tin sufficient to stop electrons coming from the silver, and obtained a spectrum showing both silver and tin lines, or rather, three lines which were thus interpreted. This author did not observe that the silver lines were displaced by the re-emission from tin. Further experiments of this nature will be considered later.

Kang-Fuh-Hu was not able to obtain any corpuscular lines corresponding to the lines emitted by the rhodium anticathode of the tube he used, and he also tried in vain to find the L lines of a lead radiator.

Mention should also be made of a series of investigations,

commenced by Sadler, Beatty, and Whiddington [6], then continued by Barkla and Shearer [7] and quite recently by Lewis Simons [8], in which it was sought to measure the velocity of projection of the electrons by their range in a rarefied gas, the pressure of which was adjustable. Barkla and Shearer were led to the conclusion that all the secondary electrons, whatever their origin, had the same velocity, corresponding to a whole quantum of the incident radiation. By interposing absorption screens, Simons made this result doubtful, and, without obtaining any definite results, concluded from examination of his curves, that the intervention of subtractive terms, depending on the energy of the successive levels, was very probable.\*

**3. Experimental investigation of the magnetic spectra of secondary  $\beta$ -rays and the laws of the phenomenon.**—In the case of X-rays where the quantum of the incident radiation is of the order of tens of thousands of volts, Barkla's conclusion that all the electrons extracted from the atom by rays of frequency  $\nu$  possessed a quantum  $h\nu$  after their emission, which was already attacked by Lewis Simons, is definitely contradicted by M. de Broglie's experiments [9], the results of which may be summarised as follows, and which appear to have settled the question.

When a monochromatic beam of X-rays of frequency  $\nu$  is incident on a secondary radiator made of an element which has the values  $W_K$ ,  $W_L$ ,  $W_M$  . . . for the energies of its Bohr levels, a number of groups of secondary electrons are expelled, the energies of which are—

$$h\nu - W_K, \quad h\nu - W_L, \quad h\nu - W_M \dots$$

As in the case of luminous rays, the velocity of the secondary electrons depends only on the frequency of the exciting rays and not on their intensity.

These experiments were carried out with an arrangement similar to that used by Robinson and Rawlinson for

\* A similar relation was also suggested by Sir Ernest Rutherford for the connection between  $\beta$ - and  $\gamma$ -rays.

examining the magnetic spectrum of the velocities of the secondary  $\beta$ -rays produced by X-rays.

The apparatus (Fig. 1, Plate 7) consists of a bronze box which can be evacuated and which contains a block of lead, illustrated in Fig. 33. The whole is subjected to a uniform magnetic field normal to the plane of the figure.

The radiator MCN is composed of a thin sheet of the substance to be examined stretched on an aluminium plate AB. If the substance is not available in the form of a thin

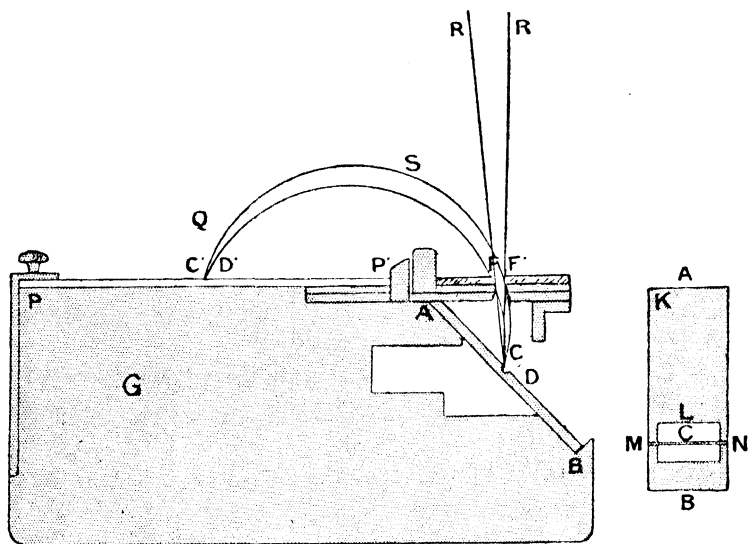


FIG. 33.

metallic sheet, strips of filter paper covered with a thin layer of oxide or other salt, or a narrow band of celluloid on which a film of the substance has been deposited by cathodic spluttering, can be employed.

This radiator is exposed to the primary rays and emits its characteristic secondary radiations, both periodic and corpuscular. The former are the fluorescent X-rays which are not deviated by a magnetic field, but which themselves act on the substance and produce secondary radiations.



The electrons projected describe circles and strike a photographic plate placed at  $PP'$  (Fig. 33).

The radiator is placed on the normal to the centre of a fairly large slit which is in the same plane as the photographic plate. The advantage of this arrangement lies in the following geometrical property :—

Let us consider all the negative corpuscles expelled from a radiator  $C$  with a given velocity  $v$ . The radius  $R$  of the circle described in the magnetic field  $H$  will be given by

$$R = \frac{mv}{He}.$$

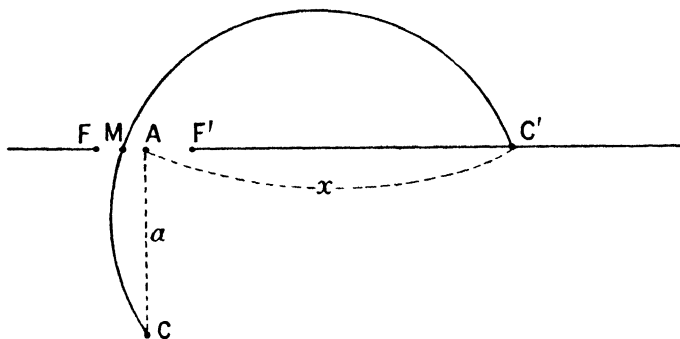


FIG. 34.

Those circles which pass through a point  $M$  of the slit (Fig. 34), such that the angle  $ACM = \phi$  will cut the plane of the slit at a second point  $C'$  situated at a distance  $x$  from  $A$ , the middle of  $FF'$ , given by

$$x = AC' = \sqrt{4R^2 \cos^2 \phi - a^2}.$$

If  $\phi$  is sufficiently small,  $x$  is independent of this angle and all the rays which pass through the slit will strike the plate at approximately the same point  $C'$ . The energy of a diverging beam, the angle of which may be fairly large is thus concentrated at this point.

The dispersion is improved if weak fields and large radii are used. M. de Broglie [15] has used an apparatus in which

the radius could be increased to about 12 centimetres, the fields being then produced with an air solenoid.

**4. Magnetic corpuscular spectra: the analysis of the levels, and the transposition of X-ray spectra.**—Let us return to the law stated at the beginning of the last paragraph; to each frequency acting on the secondary radiator (and among these must be included those of the fluorescent X-rays excited in the radiator itself) there correspond as many lines in the corpuscular spectrum as there are effective levels in the element radiated. A means is thus provided of analysing the levels and measuring their critical frequencies, which are equal to the subtractive terms in the foregoing equations, divided by  $h$ .

A monochromatic exciting radiation therefore gives rise to a corpuscular spectrum which will give a kind of analysis of the constitution of the irradiated atom, expressed in terms of its Bohr levels. On the other hand, if the electrons coming from a particular level, such as the K level, be considered, their corpuscular spectrum will depend on the composition of the incident radiation and will give a real X-ray spectrum converted into the corpuscular form, without the intervention of a crystal and without the limitations which this imposes.

In the case of rays of very high frequency, a dispersion much greater than that afforded by crystalline diffraction may be obtained easily by this method.

Figs. 2, 3, 4, 5, of Plate 7, are reproductions of corpuscular spectra (de Broglie).

Fig. 2 shows a corpuscular spectrum in which will be observed lines (marked 4) fairly widely separated produced by the  $K\alpha$  doublet of tungsten reflected by the K level of silver.

Fig. 3 is a similar spectrum showing the fluorescent silver group (1), the  $K\alpha_1\alpha_2$  doublet of tungsten (2), the  $\beta_1$  and  $\beta_2$  lines of tungsten acting on the K level of silver (3), and the  $\alpha$  doublet of tungsten acting on the L doublet of silver (4).

As an example, some experimental results will be given and compared with the predictions based on the foregoing data. Only two typical cases will be taken, but an extensive series of researches has been devoted to this line of investigation, and many substances have been examined: Zn, Sr, Mo, Rh, Ag, Sn, Sb, I, Ba, Y, Se, Cu, Au, Pb, Hg, Th, U [16].

(1) Taking Ag ( $N = 47$ ) as an example of a radiator of medium atomic number.

The above diagram (Fig. 35) shows the relative position of the lines which are produced on the photographic plate. 1, 2, and 3 are diffuse lines (having a more definite border

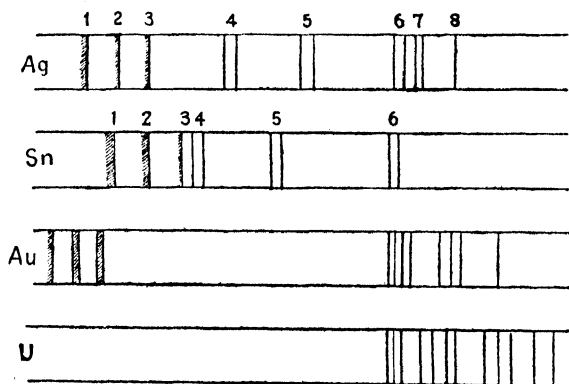


FIG. 35.

on the high energy side) which correspond to the combinations of the fluorescent lines of silver with the three L levels and the M levels. For example, line 1 should be sextuple since it corresponds to the  $\alpha_1$  and  $\alpha_2$  lines of silver combined with the three L levels of this substance.

Kossel's relation  $\beta - L = \alpha - M$  indicates that the line 2 should exhibit a complex structure containing the combinations of  $\alpha_1$  and  $\alpha_2$  with the M levels, and of  $\beta$  with the L levels. Finally, 3 corresponds to the  $\beta$  line and the M levels.

4 and 5 are the four lines of the K spectrum of tungsten, being caused by the exciting radiation combined with the

K level of silver ; these are easily distinguished by their separations and their relative intensities.

6 and 7 are due to the  $\alpha_1\alpha_2$  doublet of tungsten acting on the L and M levels of silver, and 8 to the  $\beta$  line of tungsten and the L level of silver.

The following table gives an idea of the numerical results obtained :—

TABLE XXX

Measurements \* made on the Corpuscular Spectrum of Silver  
Excited by the X-Rays of Tungsten (de Broglie)

RH Observed.	RH Calculated.†	Combination to which Attributed.
264	265	$L_1\beta_1W - L_2Ag$
320	322	$L\beta_1W - MAg$
463	463·8	$Ka_1Ag - L_2Ag$ : and $Ka_2Ag - L_1Ag$
500	500	$K\beta_1Ag - L_1Ag$
530	531·4	$K\beta_1Ag - MAg$
617	618	$Ka_2W - KAg$
631	630	$Ka_1W - KAg$
703	702	$K\beta_1W - KAg$
812	811	$Ka_2W - L_1Ag$
827	820	$Ka_1W - L_1Ag$

(2) Let us now examine another case ; that of a radiator of high atomic number such as gold. This element having a higher atomic weight than tungsten will not have its K electrons expelled by the tungsten radiations, but the greater difference in the frequencies of the L levels will cause it to give a fine structure which is more easily observed. The  $L_1$ ,  $L_2$ ,  $L_3$  levels of gold correspond, in fact, to 11,900, 13,740, and 14,360 volts and the experimental results yield the diagram shown in Fig. 35, in which the combinations of the lines of the incident beam with the levels of the radiator can be distinguished.‡

\* Too much importance should not be attached to the almost complete numerical agreement between the first two columns of this table. The measurements are accurate to 1·5 per cent. approximately, and the data used in the theoretical calculation may also involve a slight error.

† The theoretical values of RH are calculated by using the following wavelengths (Siegbahn) :

$$Ag : Ka_2 = 0\cdot56251 . Ka_1 = 0\cdot55816 . K\beta_1 = 0\cdot49597 . 10^{-8} \text{ cm.}$$

$$K \text{ limit} : 0\cdot485 . 10^{-8} \text{ cm.}$$

‡ The second and fourth diagrams of Fig. 35 indicate the structure of the corpuscular spectra given by tin and uranium radiators.

The numerical agreement between the results obtained and the laws already enunciated justifies the origin attributed to the various lines of the corpuscular spectra, but physical proofs can also be given.

Hitherto the radiator R has been considered to be exposed to the primary spectrum produced by the tube and to its own characteristic fluorescent lines. If it be desired to study other radiations, without changing the tube, the fluorescent radiations from another radiator R' can be used. The simplest way to do this is to place over the face of the radiator R which receives the primary radiation, a thin layer of a radiator R', sufficiently thick to stop corpuscles coming from R, but quite permeable to the fluorescent X-radiations from R, which are very much more penetrating.

The corpuscular spectrum received will then consist of the lines corresponding to the photo-electric effect of R' which are excited by the fluorescent rays of R, in addition to those which would be produced if R' alone were exposed to the incident radiation; that is, the electrons producing these lines will have frequencies corresponding to those of the R lines and of the incident lines corrected for the works of extraction of R'. It can easily be seen that by varying the respective values of the atomic numbers  $N$  of R and R', varied and instructive phenomena will be obtained (Fig. 4, Plate 7).

To identify the lines, a screen, which absorbs certain radiations much more strongly than others, can be interposed between the source of X-rays and the apparatus. Thus, a screen containing the oxides of the rare earths practically causes the disappearance of the  $\beta$  and  $\gamma$  lines of the K spectrum of tungsten, without unduly weakening the  $\alpha$  doublet, and enables the corpuscular lines which correspond to the absorbed rays to be eliminated.

The trajectories of the corpuscles are connected with their velocities by the relations

$$v = RH \frac{e}{m}; \quad m = \frac{m_0}{\sqrt{1 - \beta^2}},$$

whilst the kinetic energies can be expressed in terms of the velocities by the relativity formula

$$\text{Kinetic energy} = m_0 c^2 \left( \frac{1}{\sqrt{1 - \beta^2}} - 1 \right).$$

When the energy of the corpuscles is high, the difference between this formula and the ordinary expression  $\frac{1}{2}m_0 v^2$  becomes appreciable, experiment justifying the relativity formula [16]. It is interesting to note that not only is the variation of mass with velocity proved by this type of experiment, but also the validity of the preceding expression for the kinetic energy, which must be equal to the quantum.

It has been seen that by considering the corpuscular rays arising from a given level and due to the different spectral lines of the incident radiation, the spectrum of the latter can be obtained.

It might even be said that if crystalline diffraction had not been discovered, but if the conception of energy levels and Planck's laws had been known, the magnetic spectra would have led to X-ray spectra. In fact, the quantum of the superficial levels of a sufficiently light element is negligible compared with that of the K rays of tungsten. Hence, the frequency and thus the wave-length of these K rays of tungsten could have been directly determined from measurements of the magnetic field and the radii of the circles described.

The corpuscular rays arising from the more central levels of the radiator employed would have furnished, then, by their liberation, the energy of these levels (and thus the wave-length of the absorption discontinuities) so that finally, the emission and absorption X-ray spectra could have been qualitatively described and quantitatively measured without depending on crystalline diffraction.

Thus the magnetic spectra of the  $\beta$ -rays, combined with the frequencies of the X-rays, which are themselves calculated from the reticular distances of crystals, numerically verify the relations of the quantum theory.\*

\* A recent paper by Whiddington (*Phil. Mag.*, June, 1922, p. 1116) has just confirmed these results.

They also afford a remarkable justification of Bragg's hypotheses on which the estimation of wave-lengths is based ; a verification which is added to that afforded by Webster and Duane's measurements of the critical excitation voltages of the various parts of the X-ray spectrum.

**5. C. T. R. Wilson's experiment.**—Mention should be made here of an extremely striking experiment carried out by C. T. R. Wilson [20] with his well-known apparatus for registering the tracks of  $\beta$ -rays by the cloud method. A weak beam of X-rays is incident on a small copper plate at A, and a corpuscle is ejected the trajectory of which is AB. At the same time the correlative emission of a copper charac-

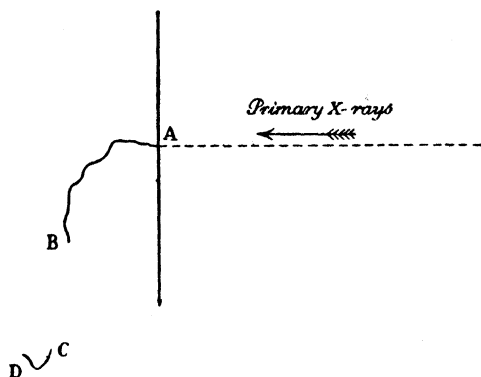


FIG. 36.

teristic ray would be expected ; if this latter is absorbed by an atom of the surrounding gas the path CD of the electron torn from this atom should also be found somewhere, and, in fact, this has been established experimentally.

Such a result emphasises in a particularly striking manner the transference of the initial energy in its various corpuscular and undulatory forms, with a localisation which is very difficult to explain on the classical wave theory.

The observation in similar experiments of the direction of the primary X-rays, that of the line AC (which represents the path of the secondary X-ray), and the directions of the initial tangents to the corpuscular trajectories AB and

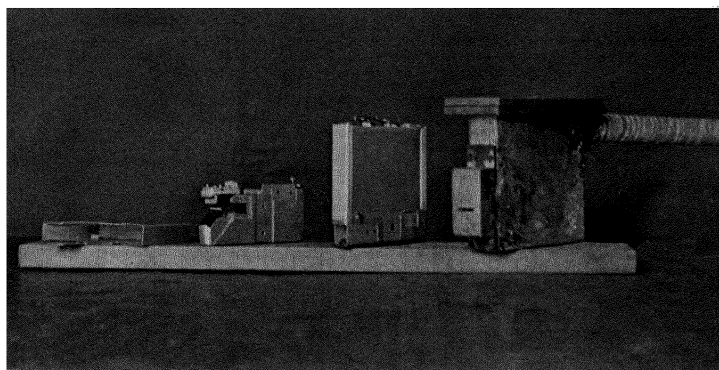


FIG. 1.—APPARATUS FOR THE MAGNETIC SPECTRA OF SECONDARY  $\beta$ -RAYS

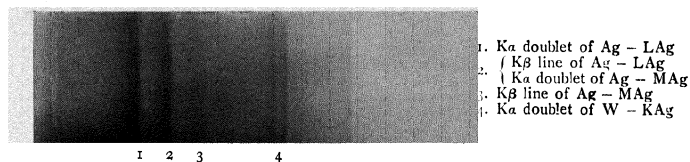


FIG. 2.—CORPUSCULAR SPECTRUM OF SILVER EXCITED BY THE K-RAYS OF TUNGSTEN

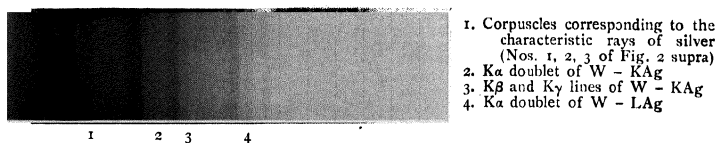


FIG. 3.—CORPUSCULAR SPECTRUM OF SILVER EXCITED BY THE K-RAYS OF TUNGSTEN

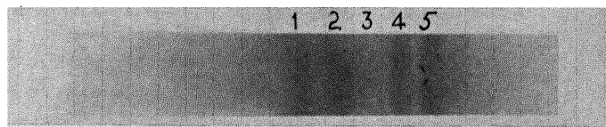


FIG. 4.—CORPUSCULAR SPECTRA OF TWO SUPERPOSED RADIATORS

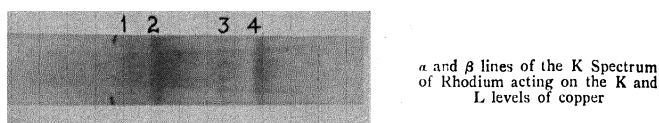


FIG. 5.—RHODIUM-COPPER CORPUSCULAR SPECTRUM





CD, together with the frequencies of the X-rays and the energies of the corpuscles, should allow to be verified whether there is indeed a conservation of the energy and of the momentum in the course of these successive transformations.

## PART II

### $\gamma$ -RAYS

#### 1. The measurement of $\gamma$ -rays by crystalline diffraction.—

The radioactive substances emit a penetrating, undeviable radiation, the relation of which to X-rays was suspected long ago (Villard). Measurements of the coefficients of absorption showed that this radiation had a wide range of penetration for different radioactive bodies, and must be, in general, very complex.

Rutherford and Andrade [10] applied de Broglie's photographic method and the one specially adapted for  $\gamma$ -rays by Sir Ernest Rutherford (p. 141) to the study of the  $\gamma$ -rays emitted by the radioactive substances which result from the disintegration of radium emanation. Considerable difficulty arises on account of the presence of fast  $\beta$ -rays emitted simultaneously or excited in a secondary way.

To eliminate fogging of the plates, it was necessary to place the apparatus in an extensive and fairly strong magnetic field (2500 gauss). The source used was a very thin glass tube containing 100 millicuries of emanation. The  $\gamma$ -rays were then due to radium B and radium C. After exposures of the order 24 hours, the plates showed numerous lines. A first group of experiments, carried out to investigate rays of medium and low penetrating power, yielded a series of lines of wave-lengths between 0.79 and 1.37 Å., that is, situated in the region of the L spectrum of heavy elements; it is well known that radium B is an isotope of lead and radium C an isotope of bismuth. A list of these lines and some data on the radiations of bismuth and lead are given in Table XXXI:—

TABLE XXXI \*

## Radium B (Ångström Units)

Soft  $\gamma$ -Rays

Intensities.†	Selective Angle at Rock Salt.	Wave- Length.	Pb(RaB) N = 82.		Bi(RaC) N = 83.	
<i>m</i>	8° 6'	0.793	0.784	<i>w</i>	0.793	<i>w</i>
<i>m</i>	8° 16'	0.809	0.814	<i>w</i>	0.8106	<i>w</i>
<i>m</i>	8° 34'	0.838	0.837	<i>m</i>	0.8378	<i>m</i>
<i>m</i>	8° 43'	0.853	—	—	—	—
<i>w</i>	9° 23'	0.917	—	—	0.922	<i>w</i>
<i>m</i>	9° 45'	0.953	0.950	<i>m</i>	0.953 — 0.949	<i>s</i>
<i>s</i>	10° 3'	0.982	0.980	<i>s</i>	—	—
<i>m</i>	10° 18'	1.006	1.005	<i>w</i>	—	—
<i>m</i>	10° 32'	1.029	1.019	<i>w</i>	—	—
<i>w</i>	10° 48'	1.055	—	—	1.057	<i>w</i>
<i>w</i>	11° 0'	1.074	1.090	<i>w</i>	—	—
<i>w</i>	11° 17'	1.100	—	—	—	—
<i>m</i>	11° 42'	1.141	—	—	1.141	<i>s</i>
<i>s</i>	12° 3'	1.175	1.172	<i>s</i>	—	—
<i>m</i>	12° 16'	1.196	1.183	<i>m</i>	—	—
<i>w</i>	12° 31'	1.219	—	—	—	—
<i>w</i>	13° 0'	1.266	—	—	—	—
<i>w</i>	13° 14'	1.286	—	—	—	—
<i>w</i>	13° 31'	1.315	—	—	1.313	<i>m</i>
<i>m</i>	13° 52'	1.349	1.346	<i>m</i>	—	—
<i>m</i>	14° 2'	1.365	—	—	—	—

A second series of experiments, devoted to the exploration of small angles gave the following results for the spectra of penetrating rays from radium B and radium C:—

TABLE XXXII

Angle of Reflection at Rock Salt.		Wave-length.
B	1° 44'	0.072 Å
	1° 0'	0.099
	1° 11'	0.116
	1° 24'	0.137
A	1° 37'	0.159
	1° 43'	0.169
	2° 0'	0.196
	2° 28'	0.242
	2° 40'	0.262
	3° 0'	0.296
	3° 18'	0.324
	4° 0'	0.393
	4° 22'	0.428

\* Sir E. Rutherford and E. da C. Andrade, *Phil. Mag.*, 1914, 1, p. 861.† *s* = strong; *m* = medium; *w* = weak.

The K spectra of the elements whose L lines appear in the preceding table, are to be expected in this region. The two strong lines marked A correspond to the positions of the most intense K lines of the elements 82 and 83 (lead and bismuth) ; the higher orders of line B of which the wave-length is  $0.099 \text{ \AA}$ . would give apparent wave-lengths at  $0.198$ ,  $0.297$ ,  $0.396$ , which are very near lines obtained ; perhaps also,  $0.324$  is the second order of the A doublet.

The lines of shorter wave-length in Table XXXII cannot be those of the K series of any known element, the K band of uranium having a wave-length of  $0.105 \text{ \AA}$ . They represent, therefore, new types of radiations which perhaps only exist for substances undergoing radioactive disintegration.

The value  $0.07 \text{ \AA}$ . is certainly far from the lowest present ; the active deposit of emanation, in fact, emits much more penetrating radiations, the wave-length of which would be perhaps one-tenth of this value.

Kovarik [12] has recently repeated Rutherford and Andrade's experiments, but he used a calcite crystal and a special ionisation apparatus for detecting the rays, which consisted essentially of a point raised to a high potential in air at atmospheric pressure.

The source employed was a small quantity of solid radium salt placed at the centre of a very thick block of lead.

Kovarik was able to find Rutherford's principal lines, but he also found other lines of greater frequency. He mentions the following :—

TABLE XXXIII

Angles of Reflection at Calcite.	Wave-length in $\text{\AA}$ .*	Quantum in Volts.
41' (corresponding to 43' at NaCl).	0.072	170,000
37.5'	0.066	187,000
33'	0.058	212,500
27.5'	0.048	255,000
21	0.037	333,600
16	0.028	437,700

\* Assuming that it is still permissible to apply the formula  $\lambda = 2d \sin \alpha$ .

## 2. Determination of the wave-length of $\gamma$ -rays by means of their secondary $\beta$ -rays and of the works of extraction.—

When the wave-length becomes very small the angles of selective reflection are also very small and the ordinary methods are no longer suitable. Ellis [13] has examined the magnetic spectrum of the  $\beta$ -rays, excited by the rays from a thin tube of radium emanation, in secondary radiators made of several heavy metals. His results show that the laws enunciated by de Broglie for X-rays still hold for  $\beta$ -rays of high velocities and for  $\gamma$ -rays. The wave-length of the latter can be deduced from the results.

The method is always that which has been described above for the measurement of the magnetic spectrum of  $\beta$ -rays, but the secondary radiator is replaced by an emanation tube covered with a sheet, or a preparation, of the element to be examined. With uranium, platinum, lead and tungsten, three strong lines are observed in the magnetic spectrum which are regularly displaced as the atomic number changes. Let the movement of one of these lines be followed; the corresponding energy can be calculated, in volts for example, and values are obtained which differ by exactly the same amount as the energies of extraction of the K levels of the element used. In other words, the same result is always obtained by adding the energies of extraction of the K levels, of uranium, platinum, etc., to the energy of the corresponding lines. This result can be interpreted as the product  $h\nu$  for the particular  $\gamma$ -ray of frequency  $\nu$  which excites the  $\beta$ -rays.

TABLE XXXIV

Metal.	Energy of the $\beta$ -rays. Volts.	K Work of Extraction.	Column 2 + Column 3.
Tungsten . . . .	166,000	69,000	235,000
	220,000	"	289,000
	276,000	"	345,000
Platinum . . . .	158,000	78,000	236,000
	212,000	"	290,000
	269,000	"	347,000
Lead . . . . .	149,000	89,000	238,000
	203,000	"	292,000
	260,000	"	349,000
Uranium . . . .	122,000	118,000	240,000
	174,000	"	292,000
	231,000	"	349,000

It therefore appears legitimate to conclude that three radiations have been discovered in the  $\gamma$  spectrum of radium emanation. These are :—

Quantum.	Wave-length.
238,000 volts.	0.0519 Å
292,000 "	0.0423 Å
349,000 "	0.0354 Å

From slightly less certain measurements, Ellis was led to assume the presence of three other components which correspond to the following values :—

253,000 volts.	364,000 volts.	400,000 volts.
0.0488 Å.	0.0399 Å.	0.0308 Å.

Radium B and radium C emit a *natural  $\beta$ -ray spectrum*, and it is logical to suppose that at least part of this spectrum is due to the secondary action of the  $\gamma$ -rays emitted by the same substance on the levels of the other atoms present. Ellis showed that eleven lines in the  $\beta$ -ray spectrum of radium B could be explained by combining the  $\gamma$ -rays previously found with the K and  $L_3$  levels of this element.

In another paper [13] the same author has investigated the  $\gamma$ -rays from radium C and gives the following results :—

Intensity..	Energies in Volts.	Wave-length in Å.
Medium . . . . .	274,000	0·0450
Feeble . . . . .	496,000	0·0249
Feeble . . . . .	583,000	0·0212
Strong . . . . .	607,000	0·0203

For thorium D only the indications yielded by the examination of the natural  $\beta$ -ray spectrum can be used, and this leads to the conclusion that the  $\gamma$  radiation is constituted as follows :—

Quantum in Volts.	Wave-length in Å.	Quantum in Volts.	Wave-length in Å.
40,800	0·302	254,000	0·0486
56,000	0·220	274,000	0·0450
206,000	0·0599	286,000	0·0431
228,000	0·0541	511,000	0·0241
248,000	0·0498	654,000	0·0189

An attempt can be made to go further, to see whether the principle of combination applies to the  $\gamma$ -rays discovered.

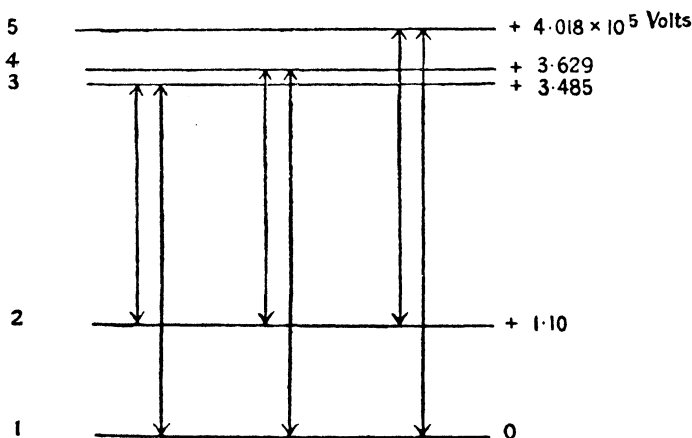


FIG. 37.

This would enable them to be attributed to the transfer of electrons between particular levels, as in the case of X-rays.

The results for radium B are fairly well explained if the levels illustrated in Fig. 37 are assumed.

It is evident, however, that the levels thus discovered no longer belong to the Bohr series of levels, on which the  $N$  electrons which surround the nucleus are arranged, because they are mostly far from the positions of the K levels. For uranium, in fact, the K level corresponds to 117,000 volts, so that these levels, which are characterised by works of extraction of several hundred thousand volts, can only be *intranuclear levels*.

The foregoing considerations therefore appear to justify the belief that stratified levels exist in the nucleus itself, between which exchanges of electrons can take place, such exchanges still obeying the laws of the quantum theory.

Miss Meitner [14] has carried out similar investigations, notably on thorium, developing a slightly different point of view which assumes that in the natural  $\beta$ -ray spectrum there are two types of  $\beta$  corpuscles; one due to the photo-electric effect of the  $\gamma$ -rays, and the other proceeding from the nucleus itself, and accompanied by a  $\gamma$ -radiation of the same quantum value. It is too soon, as yet, to be able to state definite conclusions, but the researches mentioned clearly show that a very important and fertile path has been opened for the investigation of high-frequency rays and the central regions of the atom from which they proceed.

## BIBLIOGRAPHY

1. CURIE and SAGNAC, *Comptes Rendus*, 1900, 130, p. 1013.
2. INNES, *Proc. Roy. Soc.*, 1907, p. 442.  
BESTELMEYER, *Ann. der Phys.*, 1907.
3. BEATTY, *Proc. Camb. Phil. Soc.*, 1911, p. 416.  
R. POHL. See his book, "*Physique des Rayons X*," Chapter VII, Braunschweig, 1912.
4. ROBINSON and RAWLINSON, *Phil. Mag.*, 1914, 2, p. 277.
5. KANG FUH HU, *Phys. Rev.*, 1918, 1, p. 505.
6. SADLER, BEATTY, *Phil. Mag.*, 1910 and 1912.  
WHIDDINGTON, *Proc. Roy. Soc.*, Jan. 1912.
7. BARKLA and SHEARER, *Phil. Mag.*, 1915, 2, p. 745.  
BARKLA, *Phil. Trans.*, 1917; *Bakerian lecture*.



8. LEWIS SIMONS, *Phil. Mag.*, 1921, 1, p. 120.
9. M. DE BROGLIE, *Comptes Rendus*, 1921, 1, pp. 274, 527, 746, and 806; 1921, 2, p. 1157, *Journal de Physique*, Sept. 1921, p. 265.  
M. and L. DE BROGLIE, *Comptes Rendus*, 1921, 2, p. 527.
10. RUTHERFORD and ANDRADE, *Phil. Mag.*, 1914, 1, p. 835; 1914 2, p. 263.
11. SIEGBAHN, *Jahrbuch d. Rad. und Elektr.*, Sept. 1916, XIII, 3.
12. KOVARIK, *Phys. Rev.*, 1919, 1, p. 272, and 1922, 1, p. 433.
13. ELLIS, *Proc. Roy. Soc.*, 1921, 99, p. 261, and 1922, 101, p. 1.
14. MISS MEITNER, *Zeits. für Phys.*, 1922, IX, 3, p. 131.
15. M. DE BROGLIE, *Comptes Rendus*, 1922, 1, p. 939; and *Soc. de Phys.*, 19 May, 1922.
16. M. DE BROGLIE, *Journal de Physique*, Sept. 1921, p. 265.
17. WHIDDINGTON, *Phil. Mag.*, 1922, 1, p. 1116.
18. COMPTON, *Phil. Mag.*, 1921, 1, p. 770.
19. KOVARIK, *Phys. Rev.*, 1919, 2, p. 179.
20. C. T. R. WILSON, *Proc. Roy. Soc.*, 1923, vol. 104.

## CHAPTER VII

### CONCLUDING REMARKS

THE aspect of the branch of physics, still so new, to which the pages of this book have been devoted must evolve and must undergo numerous changes in the next few years. Certain points seem to be well established, such as the rôle of Bohr's atom model, the importance of energy levels, the principle of combination, the intervention of quanta in the excitation of lines and of the continuous spectrum, Moseley's law, the connection between X-ray spectra and corpuscular spectra. Other observations, however, show that our ignorance is still profound ; perhaps it will not be useless to indicate some of these.

A spherical wave of X-rays \* in a gas, travelling outwards so that the radius increases, is known to lose energy by absorption and it can be stated that :—

(1) Only a very small number of the molecules over which the wave passes are ionised and lose fast-moving electrons.

(2) The energy of an electron thus expelled from an atom is very much greater than that which the atom could take up from the portion of the wave in its immediate neighbourhood.

We are, therefore, led to the conclusion either that the atom must be in a particularly receptive state in order to be ionised or that the distribution of energy is not uniform over the spherical surface of the wave. The manner in which energy of frequency  $\nu$  is taken up by the atom so that

\* See in particular, Sir William Bragg, *Study on Radioactivity*.

a corpuscle of energy  $h\nu$  is ejected is still quite unknown. Nor is it understood why, if the energy of the corpuscle were derived from the internal energy of the atom, this should be so definitely related to the frequency of the incident wave, since the latter would then only act as a trigger to release the electron. The same considerations can be applied to the photoelectric effect of X-rays with respect to solid bodies. The fundamental fact is that the velocities of the expelled electrons always depend on the frequency of the radiation and not on its intensity.

If it be necessary to assume, as has been sometimes suggested (Sir Joseph Thomson), that the energy is localised at certain points of the wave front, we are very near to a corpuscular theory of light.

Bohr's theory, so valuable for the representation of the emission and absorption of spectral lines, yields no information concerning the emission and absorption of the continuous spectra which are nevertheless among the principal features of radiation phenomena. Even in the case of lines it does not define in any way the mechanism whereby the exchanges of energy are effected.

The stoppage of electrons by matter and the radiations which result therefrom are worthy of more detailed investigation than they have hitherto received. In particular, it is probable that the absorption of electrons by the atoms of an element exhibits discontinuities similar to those found in the absorption of X-rays. The absorption of electrons by a screen is much more complicated than that of a periodic radiation in which case merely an approximately isotropic scattering and a diminution in the energy of the transmitted beam are usually observed. With electrons, the number of corpuscles, their individual energies, and the distribution of the directions of their velocities must be taken into account. The simple fact that very much the greater part of the energy of the cathode rays which strike an anticathode is

finally transformed into heat is far from being satisfactorily explained.

Intentionally, throughout this book stress has not been laid on the form and arrangement of the Bohr-Sommerfeld electronic trajectories because there still seem to be many difficulties in this direction, and, at present, the idea of energy levels appears to be the surest guide.

There are also some questions, of secondary importance, concerning nomenclature.

It would be useful, perhaps, to define exactly the region of wave-lengths covered by the term X-rays. If this term be confined to the lines of the series arising from the deep levels it is necessary to include in it the ultra-violet and even the visible region, since the ultra-violet series of hydrogen is the K series, and the Balmer series is the L series of this gas.

Perhaps the term could be limited on the long wave-length side by using it to designate those radiations which obey Bragg and Peirce's law of absorption, and on the short wave-length side by confining it to wave-lengths greater than that of the K limit of uranium,  $\gamma$ -rays being shorter than this.

A similar question also arises in the case of electrons in motion. When their velocity is great they are called  $\beta$ -rays, but at what energy does this term commence to apply? It is now established that some, at least of the  $\beta$ -rays from radioactive substances are electrons which come from the Bohr levels, and are not essentially different from photo-electric corpuscles.

The nomenclature of the lines in X-ray spectra is also in need of some unification. It would appear logical to denote them by the letters of the levels to which they are attributed by the principle of combination. For example, the lines of the K series would be

$$L_1K, L_2K, \dots M_1K \dots$$

but then it would be necessary to codify these designations of the levels.

When spark lines, which evolve virtual levels unoccupied in the normal state of the atom, are considered, complications will arise.

To a large extent the special properties of X-rays are due to the fact that they are very far from being in equilibrium with the temperature of the laboratory and from the conditions of reversibility which an equilibrium involves.

In the case of black body radiation at a given temperature  $T$  the density  $\rho(\nu)$  of the radiation of frequency  $\nu$  is given by

$$\rho(\nu) = \frac{8\pi h}{c^3} \nu^3 \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

and, for obtainable temperatures this leads to extraordinarily low densities for X-ray frequencies. Conversely, a beam of X-rays such as is obtained experimentally would indicate a temperature of several million degrees.

The effect of temperature can also be viewed from another standpoint; it determines the probability that the atom is more or less removed from the normal state which corresponds to absolute zero, i.e. that it is more or less ionised.

For this reason the atoms in the interior of the stars may have lost some of their exterior electronic layers and may be in a state which confers on them peculiar properties. Eddington thinks that the temperature and pressure in the central parts of some stars may exceed a million degrees and a million atmospheres. In these places X-rays will be approximately in thermal equilibrium, and their properties will be very different from those which are recorded by our terrestrial observations.

The most recent measurements of the wave-lengths of  $\gamma$ -rays suggest that the nucleus of the atom itself contains electrons, arranged on energy levels. This raises many im-

portant questions. If an attempt is made to express the energies of these levels in terms of an atomic number  $N$  this will not be the atomic number of the element given by Bohr's peripheral electrons, but a larger number which would become the ordinary  $N$  in consequence of the effect of the screen of electrons in the nucleus; at the same time, the quantum number should become unity for the K ring, which acts as the first external ring. Perhaps it might not be impossible to extract electrons from the intranuclear levels by means of X-rays of very high frequency. That would be a very important first step towards the artificial production of radioactive phenomena.

For some time now attention has been drawn by several facts to theories of light based on emission hypotheses; but, on the other hand, it should not be forgotten that innumerable phenomena, the details of which can be so well interpreted by interference, have not hitherto been satisfactorily explained except by the wave theory. Even the diffraction of X-rays may be counted as a new success for the classical theory of optics.

Nevertheless a large group of experimental facts, the importance and general character of which increases every day, require quantum considerations. For the present the physics of radiations evades all attempts at explanation by a single theory.



## APPENDIX I

### THE REFRACTION AND TOTAL REFLECTION OF X-RAYS

*The existence of a refractive index for X-Rays.*—The interference theory of Laue and that of Bragg do not in any way necessitate that, in the passage of radiation through crystals, the rays should be subject to a modification of the velocity of propagation which would correspond to the existence of a refractive index different from unity. In fact the early investigations of Röntgen, Perrin, Walter, and Chapman, and the more recent ones of Barkla, Webster and Clark, and Dauvillier had shown that the difference  $\delta$  between the index and unity was extremely small (less than  $10^{-4}$ ).

Experiment has shown, however, that Bragg's law

$$n\lambda = 2d \sin \theta_n \quad . \quad . \quad . \quad (1)$$

is only true to a first approximation, and that the angles  $\theta$  of selective reflection corresponding to successive values of  $n$  deviate systematically from the theoretical values.

Darwin and Ewald have called attention to the fact that such would indeed be the result to which the existence of a refractive index, slightly different from unity, would lead.

If a refractive index  $\mu$  were taken into account in the establishment of formula (1), Snell's or Descartes' law being

then written  $\mu = \frac{\cos \theta}{\cos \theta'}$ , it would lead to the formula

$$n\lambda = 2d \sqrt{\mu^2 - \cos^2 \theta_n} \quad . \quad . \quad . \quad (2)$$

of which (1) is the particular case for  $\mu = 1$ . From this it can be deduced that approximately

$$n\lambda = 2d \sin \theta \left( 1 - \frac{\delta}{\sin^2 \theta} \right) \quad . \quad . \quad (3)$$

if  $\mu$  is very nearly 1.

The Drude-Lorentz theory gives for the value of

$$\delta = 1 - \mu = \sum_{191} \frac{N_1 e^2}{2\pi m(\nu^2 - \nu_1^2)} \quad . \quad . \quad (4)$$



where  $\nu_1$  is a period characteristic of the substance traversed and  $N_1$  the number of resonators per unit volume which possess this frequency. If it be assumed that the incident frequency  $\nu$  is much greater than all the characteristic frequencies of the medium traversed, this can be written

$$\delta = \frac{Ne^2}{2\pi m \nu^2}.$$

But  $\nu = \frac{c}{\lambda}$ , and, to a first approximation,  $n\lambda = 2d \sin \theta_n$  so that

$$\delta = \frac{4N^2 e^2 d^2 \sin^2 \theta_n}{2\pi m n^2 c^2},$$

or finally, by (3)

$$n\lambda = 2d \sin \theta_n \left( 1 - \frac{4Ne^2 d^2}{2\pi m n^2 c^2} \right) \quad (5)$$

Hjalmar \* has shown by very accurate experiments that the expression

$$\log \frac{\sin \theta_n}{n},$$

for a given wave-length decreases, and tends towards a limit, as  $n$  increases (he made measurements up to the tenth order), and this fact is in good agreement with the relation (5).

*Anomalous dispersion.*—If a particular order of reflection  $n$  be observed and the wave-length varied, this relation (5) becomes

$$\frac{n\lambda}{\sin \theta_n} = 2Kd.$$

M. Siegbahn and his collaborators have measured the ratio

$$\frac{\sin \theta \text{ (calcite)}}{\sin \theta \text{ (gypsum)}}$$

for the first order and for various wave-lengths. This ratio, instead of being constant, was found to vary with  $\lambda$  according to a curve which presented discontinuities when the absorption wave-lengths of calcium and sulphur were traversed. This indicates that in the Lorentz equation the

\* Hjalmar, *Zeits. für Physik*, 1923, 15, p. 63.

frequencies characteristic of the substance traversed can no longer be neglected. Anomalous dispersion is therefore demonstrated.

*Total reflection.*—The existence of a refractive index slightly less than unity also involves the existence of total reflection at angles less than a given angle, which is very small if  $\delta$  is small. The expression (2) shows that this grazing critical angle  $\theta$  is such that

$$\cos \theta = \mu = 1 - \delta,$$

or approximately

$$\sin \theta = \sqrt{2\delta}$$

Obviously the phenomenon is not limited to crystalline substances; it occurs, for example, with glass and it has been observed by Compton \* as well as by Siegbahn and Larsson.

The following are some of the values which have been obtained :—

Reflecting Surface.	$\lambda$ in Å.	Critical Angle.	$\delta = 1 - \mu$ .
Glass . . .	1·279	10'	$4\cdot2 \cdot 10^{-6}$
" . . .	0·52	4'	$0\cdot9 \cdot 10^{-6}$
Silver . . .	1·279	22·5'	$21\cdot5 \cdot 10^{-6}$

The index approaches unity as the wave-length *diminishes*, and by Lorentz's formula the value of  $\delta$  can be connected with the number of electrons called into play. This may become the basis of very interesting investigations.

The reflection appears to be absolutely total within the critical angle; it diminishes very rapidly when this is passed, and is limited to a very restricted region of grazing rays.

*Refraction.*—Siegbahn and Larsson have been able to observe the prismatic deviation of X-Rays, and to obtain the spectrum of a heterogeneous beam, consisting of the K rays of iron and copper, by making it incident, at a grazing angle, in the immediate neighbourhood of the apex of a rectangular glass prism. The adjustment is difficult, but

\* A. H. Compton, *Phil. Mag.*, June, 1923.

this beautiful experiment makes the optics of Röntgen rays connect up very closely with luminous optics.

The following table gives some values of  $\delta$  for glass which Siegbahn, Larsson and Waller have obtained by this method :—

Line.	Wave-length.	$\delta, 10^{-6}$ .	$\delta/\lambda^2, 10^{-6}$ .
FeK $\alpha_{13}$ . .	1.933 Å	12.38 $\pm$ 0.4	3.31 $\pm$ 0.10
FeK $\beta$ . .	1.750 „	10.00 $\pm$ 0.4	3.26 $\pm$ 0.10
CuK $\alpha_{12}$ . .	1.536 „	8.125 $\pm$ 0.05	3.435 $\pm$ 0.02
CuK $\beta$ . .	1.389 „	6.648 $\pm$ 0.05	3.443 $\pm$ 0.03
MoK $\alpha_{12}$ . .	0.708 „	1.64 $\pm$ 0.10	3.3 $\pm$ 0.2
MoK $\beta$ . .	0.630 „	1.22 $\pm$ 0.15	3.1 $\pm$ 0.4

As the figures in the last column show the value of  $\delta$  is proportional to the square of the wave-length, as is to be expected from the theory.

Several difficult problems still remain ; thus, it may be asked how the reflecting plane, polished artificially, is defined with respect to rays of such short wave-length, and above all how far it is permissible to compare the absorption discontinuities of the X-rays with a frequency characteristic of the atom. The fine structure of the edges of the discontinuities probably plays an important part in this respect.

The existence of the anomalous dispersion leads to the prediction of remarkable properties in the neighbourhood of the absorption discontinuities, where the refractive index may be very far removed from unity.

## BIBLIOGRAPHY

On the total reflection of X-rays :—

- A. P. COMPTON, *Phys. Rev.*, 1922, 20, p. 84.  
A. H. COMPTON, *Phil. Mag.*, 1923, p. 1121.  
KIRKPATRICK, *Nature*, 19 Jan. 1924, p. 98.

On the refraction of X-rays :—

- C. C. HATLEY and BERGEN DAVIS, *Phys. Rev.*, 1924, 23, p. 290.  
BERGEN DAVIS and VON NARDROFF, *Phys. Rev.*, 1924, 23, p. 291.  
R. VON NARDROFF, *Phys. Rev.*, 1924, 24, p. 143.  
HATLEY, *Phys. Rev.*, 1924, 24, p. 486.  
M. SIEGBAHN, Lecture to the *Soc. Française de Physique*, April, 1925.  
HJALMAR and SIEGBAHN, *Nature*, 17 Jan. 1925, p. 85.  
SIEGBAHN, LARSSON and WALLER, *Die Naturwissenschaften*, 26 Dec. 1924, p. 1212.

## APPENDIX II

 $\beta$ -RAY AND  $\gamma$ -RAY SPECTRA

Since the first edition of this book a quantity of new data has added to our knowledge of the spontaneous radiations emitted in the course of radioactive disintegration, principally with respect to the  $\gamma$ -rays.

Recently Jean Thibaud (1) has utilised the examination of the magnetic spectra of the secondary  $\beta$ -rays excited in various elements by the  $\gamma$ -rays (p. 180) as a perfectly general method of analysing  $\gamma$ -ray spectra, employing an apparatus of large dimensions giving a high dispersion. The secondary radiators placed in contact with the tube containing the substance emitting the  $\gamma$ -rays (radium, mesothorium) cover a wide range: uranium, lead, platinum, tungsten, cerium, antimony, tin, silver, and so on, up to copper and even to iron. He has shown that the displacement, as a function of the atomic number of the radiator, of the homologous secondary  $\beta$ -rays excited in the various elements, verifies Einstein's photo-electric relation very exactly, even in the region of the swiftest corpuscles examined, of which the kinetic energy was equivalent to a fall through two million volts. Consequently, this law holds for very high energy quanta as well as for very low ones. The following monochromatic radiations were thus shown to be present in the  $\gamma$ -ray spectra of the active products of radium and mesothorium:—

Characteristic  $\gamma$ -Ray Spectra

Substance.	Quantum in Kilovolts.	Wave-length in cm. $\times 10^{-11}$ .	Substance.	Quantum in Kilovolts.	Wave-length in cm. $\times 10^{-11}$ .
RaB .	240.9	51.3	MsTh <sub>2</sub>	333	37.1
	293.8	42		462	26.9
	352.2	35.2		913	13.5
	465.4 ?	26.5		968	12.8
RaC .	425.6	29	ThB . .	183.6	67.3
	507	24.3		235	53
	610.1	20.23		299.5	41.5
	770.5	16.3	ThC + C''	272.7	45.2
	937.6	13.15		508	24.3
	1129	10.95		583.7	21.3
	1244	9.91		796.1	15.5
	1778	6.95			

The majority of these lines are identical with those which can be deduced, with less certainty however, from the examination of the natural  $\beta$ -ray spectra emitted by the same radioactive elements, as has been done for RaB (Ellis and Skinner [2]), RaC (Rutherford, and then Ellis [3]), ThB (Ellis, Meitner [4]), and MsTh<sub>2</sub> (Black [5]). The majority of the lines observed in the natural  $\beta$ -ray spectrum are due to the secondary effect of the  $\gamma$ -rays emitted simultaneously with the disintegration.

Jean Thibaud [6] has discovered a fact which is *a priori* rather surprising, in that he has observed the excitation of the K levels of the heavy elements by  $\gamma$ -rays corresponding to approximately two million volts. In particular, a  $\gamma$ -ray of 1,778,000 volts emitted by RaC was transformed by the L levels, of energy 140 times less than its own. Similarly, the photo-electric effect of the  $\gamma$ -rays was exhibited with a quite appreciable intensity by the K levels of lighter elements such as cerium, antimony, silver, and even of copper and iron.

Finally, the intensities of the lines of the natural  $\beta$ -ray spectrum (of RaB, for example) is about ten times greater than that of the corresponding lines of the spectrum excited photo-electrically in the element of the same atomic number (lead). This fact is to be connected with the predominance observed, in the secondary  $\beta$ -ray spectra of X-rays, of lines due to the fluorescent X radiations of the atoms ionised, over those due to the direct radiations (M. de Broglie and Jean Thibaud [7]), and with the results obtained by the irradiation with X-rays of a heavy gas in a Wilson expansion chamber. In fact, Pierre Auger [8] has demonstrated the presence of a tertiary photo-electron by the side of the secondary photo-electron, expelled simultaneously with the absorption of a quantum by an atom. This tertiary photo-electron apparently proceeds from the same atom and seems to be due to the reabsorption of the fluorescent radiation of the atom ionised. It would follow from this that there is a much greater probability that the atom emitting X or  $\gamma$  radiation should reabsorb and convert this radiation into photo-electrons than that this should be done by neighbouring atoms.

In order to make a direct examination of the wavelengths of the  $\gamma$ -rays of radioactive substances, by crystalline diffraction, Thibaud [9] has returned to the rotating crystal method. Using a thin crystal of rock salt and a source of

radiothorium, he has photographically recorded two intense lines at  $0\cdot168$  and  $0\cdot145$  Å. (corresponding to 73,500 and 85,000 volts, the latter coming from RdTh), and a line at  $0\cdot052$  Å. (corresponding to 235,000 volts and coming from ThB), the frequency of which is the highest yet measured accurately by this method. The same author has also found this line in his magnetic spectra of secondary  $\beta$ -rays; the excellent agreement between the values given by the two methods indicates that the  $\gamma$ -rays, like the X-rays, obey the laws of quanta (Einstein's formula) and also those of classical electromagnetic optics (diffraction).

## BIBLIOGRAPHY

1. JEAN THIBAUD, *Comptes Rendus*, 1924, 178, p. 1706; and 1924, 179, pp. 165, 1053, and 1322.
2. ELLIS and SKINNER, *Proc. Roy. Soc.*, 1924, 105A, pp. 165 and 185.
3. RUTHERFORD and ROBINSON, *Phil. Mag.*, 1913, 26, p. 71.  
ELLIS, *Proc. Camb. Phil. Soc.*, 1924, 22, p. 369.
4. ELLIS, *Proc. Roy. Soc.*, 1922, 100A, p. 1.  
L. MEITNER, *Zeits. für Physik*, 1922, II, p. 35.
5. BLACK, *Proc. Roy. Soc.*, 1924, 106A, p. 632.
6. JEAN THIBAUD, *Comptes Rendus*, 1924, 179, p. 815.
7. M. DE BROGLIE and J. THIBAUD, *Comptes Rendus*, 1925, 180, p. 179.
8. PIERRE AUGER, *Comptes Rendus*, 1925, 180, p. 65.
9. JEAN THIBAUD, *Comptes Rendus*, 1925, 180, p. 138.



## SUBJECT INDEX

- ABSORPTION**, abnormal, due to reflection, 45.  
 — by photographic film, 151.  
 — coefficient, 46, 47, 53, 54, 58, 59, 60, 61, 62, 78, 80.  
 — discontinuities, 4.  
 — — fine structure of, 65, 74.  
 — — increase of absorption at, 57, 79.  
 — — influence of external forces on, 9, 75.  
 — — number of, 65.  
 — — photography of, 150.  
 — — wave-lengths of, 62, 64, 65, 71, 72, 73, 79.  
 — due to fluorescence, 46, 54.  
 — — to scattering, 46.  
 — lines, 74.  
 — of fluorescent radiation, 196.  
 — — secondary  $\beta$ -rays, 166.  
 — theory of, 76.  
 — variation with wave-length, 54, 56.  
 — — — atomic number, 54.  
**Alkali halides**, crystal structure of, 28, 44.  
**Amorphous substances**, diffraction haloes with, 154, 156.  
**Analysis by X-rays**, 127.  
**Anomalous dispersion of X-rays**, 192.  
**Anticathode**, variation of intensity with, 89.  
**Atomic absorption coefficient**, 54, 58, 78, 80.  
 — distances in crystals, 27, 33, 34, 146, 148.  
 — electrons, arrangement of, 4, 39.  
 — — influence on scattering, 39.  
 — nature of X-rays, 1.  
 — number, 1, 39, 47.  
 — — Moseley's law, 12, 67, 68, 70, 116, 127.  
 — — variation of absorption with, 39, 54.  
 — theory, 1.  
**BETA ray spectra**, 181, 195.  
**Bragg and Peirce's law**, 54, 57, 77, 78.  
**CALCITE**, atomic distances in, 33, 148.  
**Celtium**, 127.  
**Characteristic absorption**, 46, 54.  
 — emission, 7, 20, 97, 118, 196.  
 — spectra, 98, 195.  
**Chemical state**, influence on energy levels, 75.  
**Cloud experiments**, C. T. R. Wilson, 138, 176, 196.  
**Coefficient of absorption**, 46, 47, 53, 54, 58, 59, 60, 61, 62, 78, 80.  
 — — reflection, 40, 45.  
**Combination**, principle of, 7, 117.  
**Conservation of quanta**, 20.  
**Constant of fine structure**, 12.  
 — voltage apparatus, 161.  
**Contact potential difference**, 16.  
**Continuous spectrum**, 83.  
 — — intensity in, 87.  
**Coolidge tubes**, 158.  
**Corpuscular radiation**, 18, 122, 165, 176, 180, 195.  
**Correspondence**, principle of, 66.  
**Critical absorption frequencies**, 1, 4, 9, 62, 65, 67, 74, 75.  
 — — — measurement of, 62, 171.  
 — excitation potential, 98.  
**Crystal faces**, 29.  
 — structure, 25, 28.  
 — — of alkali halides, 29, 44.  
**Crystals**, abnormal absorption in, 45.  
**DIFFRACTION** by amorphous substances, 154.  
 — haloes, 40, 44, 153, 154.  
 — of X-rays, 24, 37, 128.  
 — —  $\gamma$ -rays, 177.  
**Discontinuities**, absorption. (See Absorption discontinuities.)  
**Dispersion**, anomalous, 192.  
 — of X-ray spectra, 149.  
**Doublets**, irregular, 66.  
 — regular, 12, 66, 102.  
**EFFICIENCY** of an X-ray tube, 91.  
**Electromagnetic theory of X-rays**, 88, 92.  
**Electron**, annular structure of, 48.  
**Electrons in the atom**, arrangement of, 4, 39.  
 — — — influence on scattering, 39.



Elements, periodic table of, 3.  
 Emission frequency, 2.  
 — of radiation, 2, 7, 83, 91, 97.  
 Energy levels, analysis of, 171.  
 — — definition of, 2.  
 — — distribution of electrons between, 4, 116.  
 — — influence of chemical state on, 75.  
 — — intranuclear, 183, 189.  
 — — number of, 66.  
 Extraction, work of, 2, 10, 63.  
  
 FINE structure constant, 12.  
 — — doublets, 66.  
 — — of absorption discontinuities, 65, 74.  
 Fluorescent absorption, 46, 54.  
 — radiation, 20, 98, 118, 196.  
  
 GAMMA rays, wave-lengths of, 16, 141, 177, 180, 181, 195, 197.  
 General radiation, 83.  
  
 HAFNIUM, 128.  
 Haloes with amorphous substances, 154, 156.  
 Halogen alkalies, crystal structure of, 28, 44.  
 Halo method of analysis, 153.  
 High-tension apparatus, 161.  
 Hot cathode tubes, 158.  
 Hydrogen, Balmer series of, 6, 110.  
  
 INTENSIFYING screens, 152.  
 Intensity of continuous spectrum, 87, 89.  
 — of emission lines, 8, 98, 100.  
 — variation with anticathode, 90.  
 — — — azimuth, 95.  
 — — — voltage, 91, 98.  
 Interatomic distances, determination of, 27, 33.  
 — — values of, 34, 148.  
 Intranuclear levels, 183, 189.  
 Ionisation by X-rays, 138, 185.  
 — potential, 22.  
 — spectrometers, 136, 179.  
 Ionised atom, definition of, 6.  
 Irregular doublets, 66.  
 Isotopes, spectra of, 116, 178.  
  
 J TRANSFORMATION, 69.  
  
 K DISCONTINUITIES, 64, 65, 67.  
 K series, 8, 10, 102, 130.  
  
 L DISCONTINUITIES, 70, 71, 72.  
 L levels of gold, 174.  
 L series, 10, 107, 110, 113, 114, 130.  
 Laue photographs, 24.

Levels, energy. (See Energy levels.)  
 Lilienfeld tubes, 158.  
 Line spectra, emission of, 2, 7, 97.  
 — — intensity of, 8, 98, 100.  
 Liquid crystals, 157.  
 Liquids, molecular distances in, 157.  
 Lithium fluoride, crystal structure of, 44.  
 Long wave-length X-rays, 80, 121, 141.  
  
 M DISCONTINUITIES, 73.  
 M series, 110, 112.  
 Magnetic spectra, 166, 168, 171, 195.  
 — — of fluorescent rays, 174, 196.  
 — — laws of, 168.  
 Mass absorption coefficients, 54, 58, 59.  
 — — — theory of, 77.  
 Metallic films, crystal structure of, 155.  
 — sheets, crystal structure of, 154.  
 Metal threads, crystal structure of, 156.  
 Mica spectrometers, 145.  
 Molecular distances in liquids, 157.  
 Momentum of radiation, 18.  
 Monochromatic radiation, production of, 155, 175.  
 Moseley's law, 12, 67, 68, 70, 116, 120, 127.  
 Muller tubes, 160.  
  
 N SERIES, 111.  
 Nomenclature of emission lines, 8, 187.  
 Non-crystalline substances, Laue diagrams of, 154, 156.  
 Nucleus, 8, 183, 189.  
  
 OPTICAL and X-ray spectra, analogy between, 110, 116, 121, 129.  
  
 PERIODIC table of the elements, 3.  
 Photoelectric phenomenon, 13, 19, 122, 165, 176, 186, 195, 196.  
 Plank's constant, 2, 9, 87.  
 — — measurement of, 86, 96.  
 Polarisation of X-rays, 91, 94.  
 Potential difference, variation of intensity with, 91, 100.  
 Principle of selection, 7, 117.  
 — — combination, 7, 116, 117.  
 — — correspondence, 66.  
  
 QUANTA of secondary  $\beta$ -rays, 168.  
 — — various radiations, table of, 16.  
 Quantised orbits, 9, 11.  
 Quantum of action, conservation of, 20.  
 — — definition of, 15.  
 — theory, 2, 9, 13.  
  
 RADIATION, theories of, 13, 89, 92.  
 Radiations, various, frequency and quanta of, 16.

- Reflection, coefficient of, 40, 45.  
 — of X-rays, 26, 40, 128, 129, 193.  
 — — — of higher orders, 149.  
 Refraction of X-rays, 191, 193.  
 Regular doublets, 12, 66, 102.  
 Reinforcing screens, 152.  
 Resolving power of X-ray spectrographs, 149.  
 Resonance potential, 22.  
 Reticular distances, determination of, 27, 33.  
 — — — values of, 34, 36, 146, 148.  
 Rock salt, bending of, 146.  
 — — — space lattice, 29, 33.  
 Rotating crystal spectrographs, 139.  
 Rydberg's frequency, 10, 68.
- SCATTERING of radiation, 20, 24.  
 — — — absorption due to, 45.  
 — — — change of wave-length due to, 48, 121.  
 — — — influence of atomic electrons on, 39.  
 — — — — — temperature on, 37.  
 Secondary  $\beta$ -rays, 122, 165, 176, 180, 195.  
 — — — absorption of, 166.  
 — X-rays, 20, 118.  
 Selection, principle of, 7, 117.  
 Series of emission lines, 8, 10, 97, 102, 107, 110, 129.  
 Short wave-length X-rays, 141.  
 Solid solutions, X-ray examination of, 155.  
 Sources of X-rays, 158.  
 Space lattices in crystals, 25, 29, 33.
- Spectra, magnetic, 166, 168, 171, 195.  
 — natural  $\beta$ -ray, 181.  
 — X-ray, 27, 83, 97, 171.  
 Spectrographs, 134, 139.
- TEMPERATURE, influence on scattering, 37.  
 Tertiary photo-electrons, 196.  
 Thermodynamics and X-rays, 77, 188.  
 Total reflection, 129, 193.  
 Tubes, X-ray, 158.
- ULTRA-VIOLET rays, 13, 37, 121.
- VACUUM spectrographs, 144.  
 Valency influence on absorption frequency, 75.  
 Velocities of secondary  $\beta$ -rays, 165, 168.  
 Virtual levels, definition of, 5.
- WAVE-LENGTH of absorption discontinuities, 62, 64, 65, 71, 72, 73.  
 — —  $\gamma$ -rays, 16, 141, 177, 180, 181, 195, 197.  
 — — X-rays, change of due to scattering, 48, 121.  
 — — — measurement of, 27, 36, 83, 97, 101, 122, 134, 145.  
 — — — variation of absorption with, 54, 56.  
 — — — — — with azimuth, 95.
- Wires, crystal structure of, 156.  
 Work of extraction, 2, 10, 63.
- X-RAY spectra, production of, 24, 83, 158, 171.

## AUTHOR INDEX

ANDRADE, 163, 177, 178, 184.

Andrews, 155, 164.

Angerer, 91, 131.

Asahara, 155, 164.

Auger, 196, 197.

BACKHURST, 38, 52.

Baeyer, 165.

Balmer, 5, 110.

Barkla, 39, 46, 51, 63, 69, 70, 81, 94,  
117, 118, 120, 121, 131, 132, 168, 183,  
191.

Barnes, 91, 131.

Barton, 132.

Bassler, 94, 95, 131.

Bauer, 23.

Bazzoni, 123, 132.

Beatty, 91, 98, 131, 132, 166, 168, 183.

Becker, 155, 164, 165.

Benoist, 69.

Berengeren, 75, 81.

Bergen Davis, 42, 43, 51, 89, 101, 131,  
194.

Bestelmeyer, 165, 183.

Birge, 36, 87, 131.

Black, 196, 197.

Blake, 63, 64, 68, 82, 86, 87, 131.

Bohr, 1, 5, 7, 9, 11, 23, 118, 128, 186.

Bosanquet, 41, 42, 43, 45, 51.

Bragg, W. H., 27, 28, 32, 51, 54, 59,  
61, 78, 81, 137, 156, 163, 164, 185.

Bragg, W. L., 25, 27, 28, 29, 32, 36, 38,  
41, 42, 43, 45, 51, 134, 135, 137, 163,  
191.

Brainin, 90, 131.

Bravais, 25.

Brillouin, 23, 39, 52, 89, 131.

Brogie, L. de, 5, 77, 82, 133, 184.

Brogie, M. de, 34, 37, 51, 63, 64, 69,  
70, 71, 75, 81, 82, 102, 103, 119, 131,  
132, 133, 136, 140, 145, 150, 152, 154,  
157, 163, 164, 168, 170, 173, 184, 196,  
197.

CABRERA, 64.

Carter, 91, 131.

Cermak, 146, 163.

Chapman, 191.

Clark, 52, 100, 132, 191.

Compton, A. H., 21, 34, 35, 41, 42, 48,  
49, 50, 51, 52, 79, 111, 120, 129, 133,  
138, 139, 164, 184, 193, 194.

Cooksey, 107, 116, 133, 139, 147, 163.

Coolidge, 158.

Copaux, 60.

Cork, 72.

Coster, 66, 72, 73, 75, 110, 112, 113, 114,  
117, 128, 132, 133.

Crowther, 46, 51.

Curie, 183.

DADOURIAN, 123, 132.

Darbord, 146.

Darwin, C. G., 41, 45, 51, 135, 137, 163,  
191.

Dauvillier, 5, 35, 66, 67, 72, 75, 81, 82,  
86, 89, 100, 103, 104, 107, 110, 117,  
120, 127, 131, 132, 133, 141, 158, 161,  
162, 191.

Davey, 156, 164.

Debierne, 156, 164.

Debye, 37, 38, 40, 44, 49, 51, 154, 156,  
164.

Dember, 123, 132.

Dershem, 103, 111, 139.

Dessauer, 47.

Dolejssek, 104, 105, 106, 111, 133.

Dorn, 91, 131, 165.

Duane, 51, 52, 63, 64, 68, 70, 71, 81,  
82, 86, 87, 90, 102, 103, 111, 116,  
117, 131, 132, 133, 138, 139, 176.

Dulong, 38.

Dunlop, 46, 51.

ELLIS, 180, 181, 184, 196, 197.

Ettisch, 155.

Ewald, 149, 163, 191.

FOOTE, 123, 124.

Fresnel, 14.

Fricke, 63, 64, 69, 74, 81, 82, 144.

Friedel, 157, 164.

Friedrich, 25, 51, 96, 132, 153, 154, 163.

Friman, 34, 144, 163.

GLOCKER, 58.

Gorton, 34, 111, 145, 163.

Gouy, 129, 133, 146, 163.

- HADDING, 156, 164.  
 Haga, 95, 132.  
 Ham, 96, 132.  
 Hatley, 194.  
 Hertz, 72, 74, 81.  
 Herweg, 95, 132.  
 Herzog, 155, 164.  
 Hevesy, 128.  
 Hewlett, 47, 51.  
 Hjalmar, 104, 105, 106, 133, 192, 194.  
 Holthusen, 47, 51.  
 Holweck, 57, 68, 75, 81, 125, 128, 132, 133.  
 Hu, 64, 82.  
 Hughes, 68, 123, 132.  
 Hull, 47, 51, 58, 86, 87, 98, 131, 154, 155, 162, 164.  
 Hunt, 86, 87, 131.  
 Hupka, 154, 163.  
  
 INNES, 165, 183.  
 Ishino, 47.  
  
 JAMES, 41, 43, 45, 51.  
 Jancke, 155, 164.  
 Jauncey, 38, 50, 52.  
 Jeans, 23.  
 Joffé, 146, 163.  
 Jonsson, 63, 64, 82, 142.  
  
 KAHLER, 155, 164.  
 Kang-Fu-Hu, 167, 183.  
 Karcher, 112.  
 Kaye, 90, 95, 119, 131, 132.  
 Keesom, 157, 164.  
 Keltmann, 100.  
 Kirchbaum, 96, 132.  
 Kirkpatrick, 91, 95, 133, 194.  
 Kossel, 7, 68, 74, 81, 117, 132, 173.  
 Kovarik, 141, 179, 184.  
 Knipping, 25, 51, 153.  
 Kramers, 80, 82, 89, 133.  
 Kuhlenskampff, 43, 89, 91, 133.  
 Kurth, 123, 132.  
  
 LADENBURG, 87, 133, 165.  
 Laird, 132.  
 Landé, 66.  
 Larsson, 193, 194.  
 Laue, 25, 38, 44, 51, 153, 191.  
 Ledoux-Lebard, 35, 86, 103, 131, 162.  
 Leide, 107.  
 Lepape, 23, 72.  
 Lilienfeld, 103, 158.  
 Lindemann, 38, 145, 163.  
 Lindh, 75, 76, 81, 82.  
 Lindsay, 72.  
 Loebe, 96, 132.  
  
 McKEEHAN, 52.  
 McKlung, 91, 131.  
  
 Malmer, 144.  
 Mauguin, 38.  
 Meitner, 183, 184, 196, 197.  
 Miller, 96, 132.  
 Millikan, 37, 110, 121, 132.  
 Mohler, 123, 124.  
 Moseley, 1, 12, 23, 34, 68, 116, 135, 136, 137, 144, 163.  
 Muller, 87, 160.  
  
 NARDROFF, 194.  
 Newton, 14.  
 Nishikawa, 155, 164.  
  
 OVERN, 111.  
 Owen, 59, 60.  
  
 PASCHEN, 12.  
 Patterson, 70, 71, 81, 102, 111.  
 Peirce, 54, 61, 78, 81.  
 Perrin, 18, 191.  
 Petit, 38.  
 Planck, 2, 13.  
 Pohl, 183.  
 Poincaré, 25.  
 Polanyi, 155, 164.  
 Poynting, 18.  
  
 RAWLINSON, 167, 168, 183.  
 Reboul, 127, 133.  
 Rice, 47, 51, 58, 98.  
 Richardson, 68, 123, 132.  
 Richtmeyer, 47, 51, 58, 61, 62, 81, 82.  
 Ritz, 129.  
 Robinson, 167, 168, 183, 197.  
 Rogers, 103.  
 Rohmann, 145, 163.  
 Röntgen, 94, 131, 191.  
 Ross, 48, 50, 52.  
 Rubinovicz, 117.  
 Russell, 47.  
 Rutherford, 86, 91, 131, 141, 163, 168, 177, 178, 184, 196, 197.  
 Rydberg, 1, 10, 129.  
  
 SADLER, 51, 168, 183.  
 Sagnac, 118, 166, 183.  
 Scherrer, 44, 51, 154, 164.  
 Seemann, 103, 142, 145, 163.  
 Shearer, 168, 183.  
 Shimizu, 64, 81, 82, 90, 103, 116, 117, 131, 132, 133.  
 Siegbahn, 34, 35, 37, 63, 64, 82, 102, 103, 105, 106, 111, 116, 133, 141, 142, 144, 145, 147, 148, 149, 161, 163, 164, 184, 193, 194.  
 Simons, 168, 184.  
 Skinner, 196, 197.  
 Smedt, de, 157, 164.  
 Smekal, 66, 81, 133.  
 Soddy, 47.

Sommerfeld, 9, 11, 23, 65, 66, 70.

Stark, 95, 132.

Stensson, 105, 106.

Stenström, 34, 64, 73, 74, 81, 82, 103,

105, 106, 112, 116, 117, 132, 133, 144.

Stoner, 5.

TAYLOR, 82.

Thibaud, 195, 196, 197.

Thomson, J. J., 39, 92, 122, 132, 186.

UHLER, 107, 139, 146, 163, 164.

Ulrey, 90, 131.

Urbain, 127.

VAN DEN BROEK, 1.

van den Lingen, 38.

Vegard, 95, 132.

Villard, 162, 177.

WAGNER, 34, 43, 51, 63, 64, 70, 71, 81,  
82, 84, 87, 91, 96, 131, 132, 133.

Waller, 194.

Walter, 94, 131, 191.

Webster, 84, 87, 89, 91, 98, 99, 100, 110,  
131, 132, 133, 139, 146, 164, 176, 191.

Weeks, 91, 131.

Wentzel, 66, 118, 133.

Whiddington, 98, 132, 168, 176, 183,  
184.

White, 69, 81.

Wien, 91, 97, 131.

Wilson, C. T. R., 21, 138, 176, 184.

Wingardh, 58, 82.

Wolfers, 50, 129, 133.

Wooten, 59, 98, 100, 101, 132.

YOSHIDA, 146, 164.

Young, 14.















